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TITLE NITROGEN - RICH OXIME COMPLEXES.

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NITROGEN-RICH OXIMIC COMPLEXES

A Thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the Degree of Doctor of Philosophy

by

George Cleovoulos Georgiou

The Polytechnic of North London in collaboration with the Royal Armament Research and Development Establishment

May 1988

For my parents

'If you do not expect it, you will not find out the unexpected'

(Heraclitus)

DECLARATION

Whilst registerd as a candidate for this degree, the author has not been registered as a candidate for any other award

G. C. Georgiou

G. C. Georgiou

NITROGEN-RICH OXIMIC COMPLEXES

Abstract

The complexing behaviour of chloroglyoxime (cgH_2), dichloroglyoxime ($dcgH_2$), and diaminoglyoxime ($dagH_2$) towards copper and nickel has been studied. The complex $Ni(cgH)_2$ has been obtained from amphi cgH_2 and nickel(II) acetate. Nickel(0) and cobalt(0) carbonyls, and copper(II) acetate reacted with $dcgH_2$ to give solids of ill-defined composition, which on treatment with pyridine gave tetrachlorometallate(II) compounds involving the 1,2-dihydroxy-1,2-di(N-pyridinium) cation. Reaction of $dagH_2$ with nickel(II) chloride in the presence of hydrochloric acid afforded the complexes $NiCl_2.dagH_2$, and $NiCl_2.2dagH_2$. An X-ray crystallographic study of $NiCl_2.2dagH_2$ indicated that the neutral ligand is chelated to the metal via the oximic nitrogen, and the amino groups are not involved in any bonding to the metal.

Several modified dioximes have been prepared by reactions of anti cgH_2 and $dcgH_2$ with compounds containing labile hydrogens. Modified dioximes have also been synthesised by reactions of $dagH_2$ with compounds containing active halogens and carbonyl groups. The mass spectra, thermal properties, and complexing behaviour of all new dioximes were studied. Various reactions involving the complexes $Cu(dagH)_2.H_2O$, and $Ni(dagH)_2$ were examined. The system involving $Ni(dagH)_2$ and 2,4,6-trinitrochlorobenzene, led to the nickel(II) complex of 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime, and $NiCl_2.dagH_2$. The analogous reaction of $Cu(dagH)_2.H_2O$ led to the copper(II) chloride adduct of 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime. The reaction of $Ni(dagH)_2$ with sodium 5-nitrotetrazolate ($NatNO_2$) involved ligand exchange, to give $Ni(tNO_2)_2.4H_2O$, which was characterised by X-ray crystallography. Similar behaviour was observed for the system involving $Ni(dagH)_2$ and 5-hydroxytetrazole. Reactions of copper(II) and nickel(II) diaminoglyoximates and diphenylglyoximates with dimethyl acetylenedicarboxylate led to 2:1 adducts involving fused N-hydroxypyrrole rings, which arise by Michael addition and cycloaddition.

The EI, isobutane PICI, and methane NICI mass spectra of all dioximes showed that fragmentation via loss of the dioxime substituent is common to most dioximes. Generally, the process of deoximation is unimportant.

Thermal studies of the dioximes showed that the unsymmetric dioximes and their complexes decompose at temperatures lower than symmetric dioximes and their complexes. In general, the copper(II) complexes decompose at lower temperatures, and have higher heats of reaction and activation energies than corresponding nickel(II) complexes.

ACKNOWLEDGEMENTS

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CONTENTS

ABBREVIATIONS

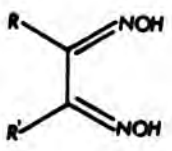
cgH_2	Chloroglyoxime
$dcgH_2$	Dichloroglyoxime
agH_2	Aminoglyoxime
$dagH_2$	Diaminoglyoxime
$dmgH_2$	Dimethylglyoxime
$dPhgH_2$	Diphenylglyoxime
$chgH_2$	Cyclohexaneglyoxime
HtH	Tetrazole
HtCl	5-Chlorotetrazole
$HtNO_2$	5-Nitrotetrazole
pcCl	2,4,6-Trinitrochlorobenzene (Picryl chloride)
salH	Salicylaldehyde
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
DME	1,2-Dimethoxyethane
DMAD	Dimethyl acetylenedicarboxylate
qoH	Any 1,2-quinone mono-oxime
PICI	Positive-ion chemical ionisation
NICI	Negative-ion chemical ionisation
DSC	Differential scanning calorimetry
TG	Thermogravimetric analysis
Ea	Activation energy
%T	(%)Transmission
%I	(%)Intensity

CHAPTER 1

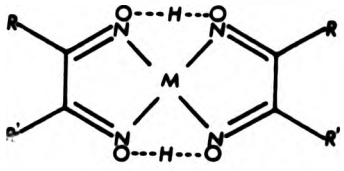
1. Metal Complexes Derived from Dioximes of 1,2-Diketones with Reactive Substituents

1.1 Introduction

Dioximes of 1,2-diketones (1.1), otherwise known as vic-dioximes, is a class of well-known compounds. In this thesis, these compounds will be referred to as glyoximes. The investigation of these compounds began over a century ago,[1] and their applicability in various fields has attracted much attention. Interest in these compounds has been mainly concerned with their reactivity towards metal ions to form metal complexes (1.2).



1.1



1.2

R, R'= e.g., H, Me, Ph

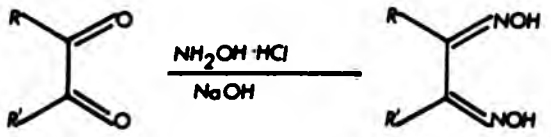
M= e.g., Cu, Ni, Pd

The chelating properties of dioximes have led to their extensive use in metal ion analysis, both qualitative and quantitative. Dimethylglyoxime (1.1: R= R'= Me), the best-known example of a vic-dioxime, is used in the analysis

and extraction of many metals.[2] Dioximato metal complexes have also found uses as dyes. Recently, cobalt complexes of dimethylglyoxime have been studied extensively as models of vitamin B_{12} and related coenzymes.[3] Iron complexes of several dioximes have been investigated because of their ability to mimic haemoglobin and myoglobin, by forming adducts with dioxygen and carbon monoxide.[4, 5]

The study of the isomeric character and reactivity of dioximes and of their metal complexes have also attracted much attention.[6-10]

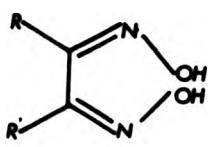
The general method of preparation of dioximes involves the treatment of 1,2-diketones with hydroxylamine (Reaction 1.1).[11] Other special methods have been applied for the synthesis of some dioximes, and these include reactions of halogenated ketones,[12, 13] and epoxy-dioxiindiols.[14]



Reaction 1.1

Symmetrically substituted dioximes (1.1; R= R') are known to exist in three isomeric forms <u>syn</u> (1.3), <u>amphi</u> (1.4), and <u>anti</u> (1.5)[15]. A fourth isomer is possible for asymmetric dioximes (1.1; R≠ R'), and this is another <u>amphi</u>

form (1.6).[16] The structures of glyoxime and dimethylglyoxime have been shown to have the anti-s-trans configuration (1.7) from X-ray work.[17, 18] In both cases, hydrogen-bonds O-H---N link molecules of the dioxime. However, for the convenience of the reader, dioximes will be schematically represented throughout this thesis as shown in 1.1.



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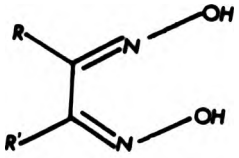

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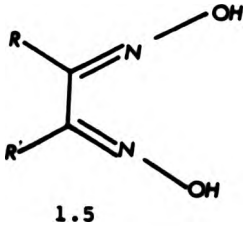

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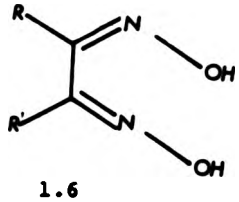

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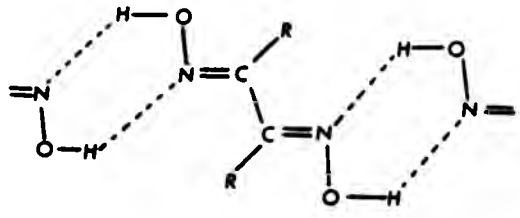


R= H, Me

1.7

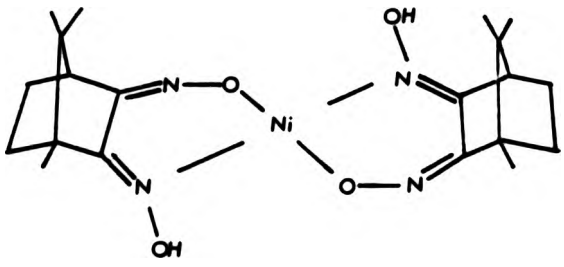
The isomeric nature of dioximes has been previously studied using absorption spectra,[19] dissociation constant measurements,[19] and metal complexation methods.[20-22] With

regard to the latter, it has been shown that dioximes with the syn configuration do not usually form metal complexes in aqueous media, in view of the ligand's geometry,[23] whereas the anti isomers give bisglyoximato complexes with metals such as nickel. The amphi form of a dioxime may lead to complexes which contain either the monoanion or the dianion of the dioxime. However, little is known about the structure of complexes containing the dianion of a dioxime.

In complexes which contain the monoanion of the dioxime, coordination of the ligand to the metal occurs mainly through the oximic nitrogen, irrespective of the type of metal, or the substituent on the dioxime. This has been established by the crystal structures of several such complexes, including $Ni(dmgH)_2$,[24] $Cu(megH)_2$,[25] $Cu_2(dmgH)_4$,[26] and $[Au(dmgH)_2]^+[AuCl_2]^-$.[27] The X-ray crystallographic study of $CuCl_2.dmgH_2$ showed that bonding of the metal through the oximic nitrogen also occurs for complexes which contain the neutral dioxime.[28] In related compounds, such as complexes derived from 1,2-quinone mono-oximes, the metal has also been shown to be almost always bonded through the oximic nitrogen. This is supported by the X-ray studies on the structures of the diacetone adduct of the copper(II) complex of 1,2-naphthoquinone 1-oxime,[29] as well as the 1:1 pyridine adduct of bis(4-methyl-1-quinone-2-oximato)-copper(II).[30]

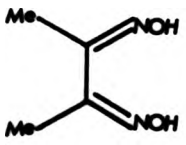
Bonding involving the oxygen atom of the oximic group has

been established by X-ray crystallography for the complex bis(camphorquinoneglyoximato)nickel(II) (1.8).[31] In this complex, chelation occurs through both the oximic nitrogen and oxygen atoms. This is because of the bicyclic nature of the ligand which increases the angle between the oximic carbon and nitrogen atoms. As a result of this, bonding through the oxygen atom involves a large ring, and is thus more favourable than bonding through both the nitrogen atoms.



1.8

Most complexation studies have been concerned with dioximes having alkyl or aryl groups (e.g., 1.9, 1.10), or with dioximes in which the oximic carbons form part of a ring (e.g., 1.11).[2, 7, 10, 32]



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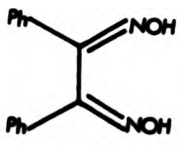

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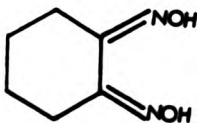
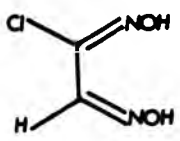


1.11

In contrast, the study of the complexing behaviour and of the chemistry of dioximes having reactive substituents such as chloro and amino (1.12 - 1.15) received considerably less attention.[33-37]



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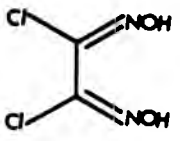

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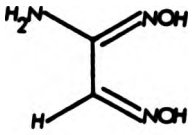

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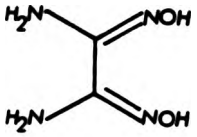


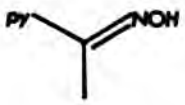
1.15

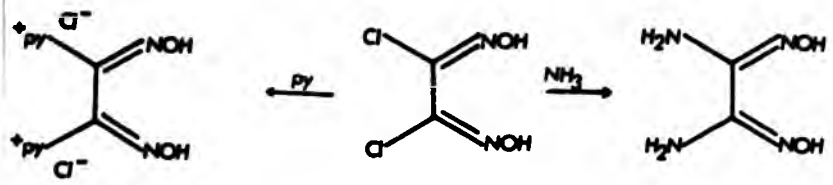
In the following sections of this chapter, the previous studies on the complexation behaviour of 1-chloro-1,2-ethanedionedioxime (1.12), 1,2-dichloro-1,2-ethanedionedioxime (1.13), and 1,2-diamino-1,2-ethanedionedioxime (1.15) are briefly reviewed and contrasted to findings obtained during the present work. These dioximes will also be referred to as chloroglyoxime, dichloroglyoxime, and diaminoglyoxime, respectively.

1.2 The Complexing Behaviour of Dichloroglyoxime, and Chloroglyoxime

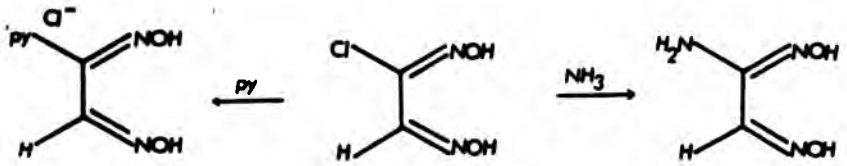
The classical method for the preparation of complexes of dioximes is the reaction of a metal salt with a dioxime in the presence of ammonia,[38] or sodium hydroxide.[39] A tertiary amine, such as pyridine, can be used instead of ammonia.[11] Generally with divalent metals, these reactions give bisglyoximato complexes containing the monoanion of the dioxime (1.2).

Dichloroglyoxime reacts with ammonia to give diaminoglyoxime, whereas with pyridine gives 1,2-dihydroxy-1,2-di(N-pyridinium) dichloride (Scheme 1.1).[40] A previous study showed that anti chloroglyoxime behaves similarly with ammonia to give aminoglyoxime,[41] and the present study has shown that this dioxime also reacts with pyridine to give 1,2-dihydroxyiminoethane-N-pyridinium chloride (Scheme 1.2).* As a consequence of this, the classical methods for the preparation of complexes of dioximes cannot be applied for the synthesis of dichloroglyoximato and chloroglyoximato complexes.

* The reaction of the chloroglyoximes with pyridine involves a nucleophilic attack by the nitrogen of the amine on the oximic carbon, which will be represented as 



Scheme 1.1

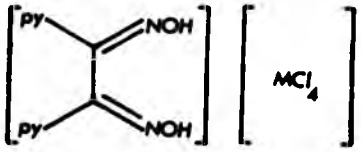


Scheme 1.2

Other methods, such as the reaction of dichloroglyoxime with a metal hydroxide in aqueous media, have been found unsuitable for the synthesis of complexes of dichloroglyoxime.[40] Furthermore, potentiometric and spectrophotometric studies of aqueous solutions of dichloroglyoxime and nickel perchlorate have indicated that hydrolysis of the dioxime occurs and a complex of dihydroxyglyoxime is formed.[42] A recent study reports on the ^{14}N NQR spectra of the nickel(II), palladium(II), and platinum(II) complexes of dichloroglyoxime, but gives no details regarding their preparation and characterisation.[43] The preparation of $Co(dcgH)_2$ by the reaction of

octacarbonyldicobalt(0) and dichloroglyoxime, and of $Cu(dcgH)_2.2H_2O$ from copper(II) acetate and dichloroglyoxime have been reported,[40] but during the present study it has not proved possible to repeat these syntheses.

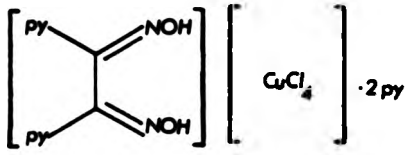
In this study it has been found that the systems $Ni(CO)_4$-$dcgH_2$, and $Co_2(CO)_8$-$dcgH_2$ do not afford the bisdichloroglyoximato $M(dcgH)_2$, but rather ill-defined solids containing one dichloroglyoxime unit per metal atom. These solids react readily with pyridine to give 1,2-dihydroxy-1,2-di-(N-pyridinium) tetrachlorometallates of type 1.16. This suggests that the solids obtained from the systems involving dichloroglyoxime with the nickel and cobalt carbonyls contain the dichloroglyoxime moiety. This is also supported by the reactions of the solids with sulphuric acid which gives free dichloroglyoxime.



1.16

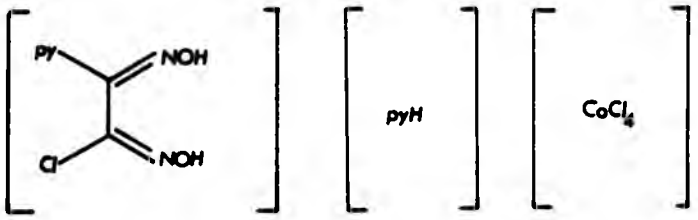
In contrast to previous reports,[40] dichloroglyoxime reacts with copper(II) acetate to give a product which contains one ligand unit per metal atom. As in the case of the

products obtained from the reaction of the dioxime with nickel and cobalt carbonyls, this copper-containing product reacts with sulphuric acid to give free dichloroglyoxime. Reaction of the copper-containing product with pyridine gives 1,2-dihydroxy-1,2-di(N-pyridinium) tetrachlorocuprate(II) dipyridine (1.17), and copper(II) chloride dipyridine.



1.17

Similar tetrachlorometallate(II) compounds, to those noted above, but containing one pyridine per dioxime moiety have been obtained previously from reactions of dichloroglyoxime and metal chlorides in the presence of pyridine.[40] The structure of one of these compounds (1.18) has been established by X-ray crystallography.[40]



1.18

Some properties for the tetrachlorometallate(II) products obtained during this study are presented in Table 1.1. All the three tetrachlorometallates show molar conductivities within the expected range for 2:1 electrolytes (115 - 250 ohm^{-1} cm^2 mol^{-1}).[44] Their i.r. spectra are quite similar. Bands due to OH stretching and bending modes appear at 3320 - 3420 cm^{-1} and 1450 cm^{-1}, respectively, and the C=N bands appear in the region of 1610 cm^{-1}.

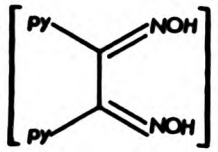
Their magnetic moments and electronic spectra reflect the tetrahedral structure of the tetrachlorometallate anions.

Table 1.1 Some Properties of the Tetrachlorometallate(II) Compounds Involving the 1,2-Dihydroxy-1,2-di(N-pyridinium) Ion (X)[1]

Compound	Melting Point (^{o}C)	Magnetic Moment (μ_B)	Molar Conductivity Λ_M(ohm^{-1} cm^2 mol^{-1})	U.V./Visible absorption data	
				λ_{max} (nm)	ϵ_{max} (m^2 mol^{-1})
$[X][CoCl_4]$	180 - 182	4.61	128	203	sh.
				250	1133
				256	1196
				262	sh.
				600	sh.
$[X][NiCl_4]$	212 - 214	3.79	132	249	sh.
				255	1813
				664	sh.

Table 1.1 (continued)

Compound	Melting Point (^{o}C)	Magnetic Moment (μ_B)	Molar Conductivity Λ_M(ohm^{-1} cm^2 mol^{-1})	U.V/Visible absorption data	
				λ_{max} (nm)	ϵ_{max} (m^2 mol^{-1})
[X][CuCl4].2py	196 - 198	1.70	119	255	3365
				256	sh.
				425	sh.
				780	broad

1: X= 

The complexation behaviour of the three isomers (*syn*, *amphi*, and *anti*) of chloroglyoxime attracted some attention in the past.[45] The preparation and isolation of the complex potassium bis(chloroglyoximato)nickel(II), from *amphi* chloroglyoxime has been reported.[45] This complex is believed to contain the dianion of the dioxime and has been formulated as $K_2[Ni(cg)_2]$. It has been found that with nickel(II) acetate, the *syn* isomer of chloroglyoxime gives a stable red complex, and the *amphi* isomer gives a yellow complex, but no formulations for either complex has been suggested.[46]

During the present study, it has been found that the reaction of *amphi* chloroglyoxime with nickel(II) acetate in aqueous methanol leads to bis(chloroglyoximato)nickel(II). This complex results in high yield. In contrast, the analogous reaction of *amphi* chloroglyoxime with copper(II) acetate gives a product having an ill-defined i.r. spectrum and metal:ligand ratio of 1:1, and *anti* chloroglyoxime reacts with both nickel(II) and copper(II) acetate to give products of ill-defined composition. Treatment of the complex $Ni(cgH)_2$ with dilute hydrochloric acid gives free *anti* chloroglyoxime. Its magnetic moment was found to be 2.92 μ_B, which suggests that the nickel is in an octahedral or tetrahedral environment. Although the majority of oximic nickel(II) complexes have been found to be diamagnetic with a square planar structure,[10, 47-49] some are paramagnetic as found during the present work (Chapter 2), and by other workers.[50]

1.3 The Complexing Behaviour of Diaminoglyoxime

Whereas chelating studies of chloroglyoxime and dichloroglyoxime in the past have been few and non-systematic, the complexation behaviour of diaminoglyoxime is better understood. Diaminoglyoxime has proved useful for analytical determinations of a number of metals. A list of selected complexes of diaminoglyoxime is given in Table 1.2. However, the structural characteristics of such complexes are, in many cases, not very clear.

Diaminoglyoxime is an important and interesting chelating agent. The chelating significance of this dioxime lies in its potential ability to chelate through different functional groups (Scheme 1.3). In addition to the structures given in Scheme 1.3 , coordination through one or both oxygen atoms of the oximic groups may occur, and the ligand can act in a neutral or anionic fashion.

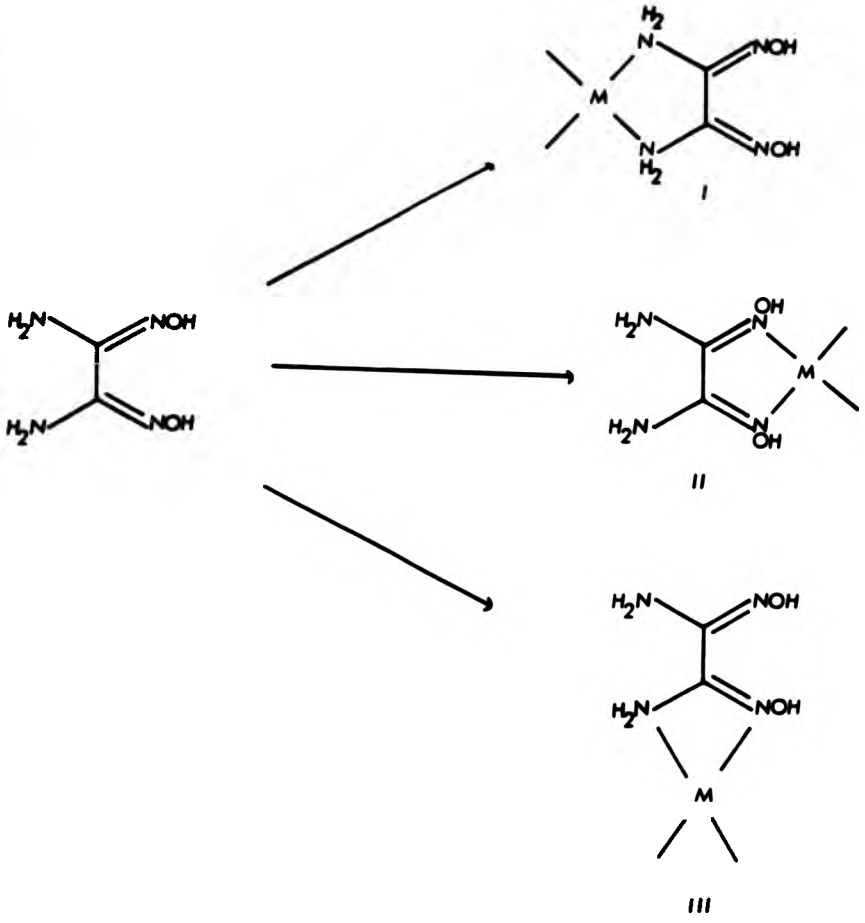
Generally, adducts of diaminoglyoxime containing the dioxime in its neutral form are prepared by the interaction of the dioxime with the appropriate salt in acidic media, whereas diaminoglyoximato complexes in which the ligand is the monoanion of the dioxime are prepared in alkaline media.

Table 1.2 Complexes of Diaminoglyoxime ($dagH_2$)

Group	Complex	Remarks	Reference
A: X-ray study shows coordination through the oximic nitrogen	$Co(dagH)_2(dagH_2)$	$DagH_2$ coordinates as as neutral and monoanionic ligand	53
	$[Co(dagH_2)_3]Cl_3$	$DagH_2$ coordinates as neutral ligand	54
	$Ni(dagH)_2(H_2O).DMF$	Solvent molecules do not participate in bonding	55
	$Ni(dagH)_2.2H_2O$	Ladder-like structure as a result of H-bridging between adjacent molecules from H_2O to oximic oxygens	56

Table 1.2 (continued)

Group	Complex	Remarks	Reference
B: Coordination is proposed to occur through the NH_2 and NOH groups	$[Co(dagH)_2(NH_3)_2]Cl$	Coordination through the amino and oximic groups is proposed on the basis of the similarity of their physical properties with those of cobaltammines	51
	$[Co(dagH)_2(py)_2]Cl$		51
C: Coordination is proposed to occur through the NH_2 groups	$CuCl_2.dagH_2$	Coordination through the amino groups is assumed on the basis of the ease of NH_2 to chelate	52
	$CuCl_2.2dagH_2$		52
	$CuSO_4.2dagH_2$		52
D: General	$Co(dagH)_2(SO_2).3H_2O$	Various other complexes of $dagH_2$	57
	$Co(dagH)_2(NO).3H_2O$		57
	$Pd(dagH)_2.H_2O$		58



Scheme 1.3

In complexes of type II, the ligand is the monoanion of the dioxime, and chelation occurs through the nitrogens of both

oximic groups. As indicated in Table 1.2, all X-ray crystallographic studies of complexes of diaminoglyoxime show that the oxime nitrogens act as the coordinating sites whether the ligand is present in its neutral or monoanionic form. In complexes of type III, both the oximic and amino nitrogens participate in bonding. For the complexes $[Co(dagH)_2(NH_3)_2]Cl$ and $[Co(dagH)_2(py)_2]Cl$ coordination is proposed to occur through the NH_2 and NOH groups of diaminoglyoxime, because of similarities of their physical properties with those of cobaltammines, but such suggestions are clearly inappropriate.[51] In complexes of type I, the ligand is in the neutral form, and chelation occurs through the nitrogens of the amino group. For the copper(II) and nickel(II) chloride adducts of diaminoglyoxime, as well as other similar adducts, bonding via the amino sites of the dioxime has been proposed, but this has not been established crystallographically.[51, 52] However, a recent X-ray study showed that for bis(diaminoglyoximato)cobalt(II)(diaminoglyoxime) ($Co(dagH)_2(dagH_2)$), chelation occurs via the oximic groups, with intermolecular bonding via the amino groups.[53]

According to a previous report, diaminoglyoxime reacts with nickel chloride in a 1:2 molar ratio in the presence of dilute hydrochloric acid to give the adduct bis(diaminoglyoxime)nickel(II) chloride hexahydrate ($NiCl_2(dagH_2)_2(H_2O)_6$).[51] This reaction has been reinvestigated during the present study, and it has been established that it leads to the anhydrous 1:2 adduct

bis(diaminoglyoxime)nickel(II) chloride (1.19). Also, the 1:1 adduct mono(diaminoglyoxime)nickel(II) chloride (1.20) was obtained from the analogous 1:1 reaction, and in the presence of dilute hydrochloric acid.

Both diaminoglyoxime adducts of nickel(II) chloride were characterised on the basis of their elemental analyses, i.r., and electronic spectra, molar conductivity measurements, and magnetic moments. In the case of bis(diaminoglyoxime)-nickel(II) chloride, an X-ray investigation confirmed its structure (Section 1.4).

The i.r. of both the anhydrous adducts are different to that of free diaminoglyoxime. In the free ligand, the absorption frequency of C=N is at 1640 cm^{-1} (Figure 1.1). However, assignment of the C=N band in the 1:1 and 1:2 adducts cannot be made with accuracy due to the presence of more than one absorption band in the region of 1600 - 1700 cm^{-1} (Figures 1.2 and 1.3). On the other hand, in the i.r. of the chelate $(Ni(dagH)_2$ (Figure 1.4), the C=N stretching vibration gives an absorption band at 1590 cm^{-1}, which is significantly lower than the corresponding C=N band in the free dioxime. The shift of the C=N band to lower frequencies upon chelation has been observed in the i.r. spectra of other dioxime complexes.[28]

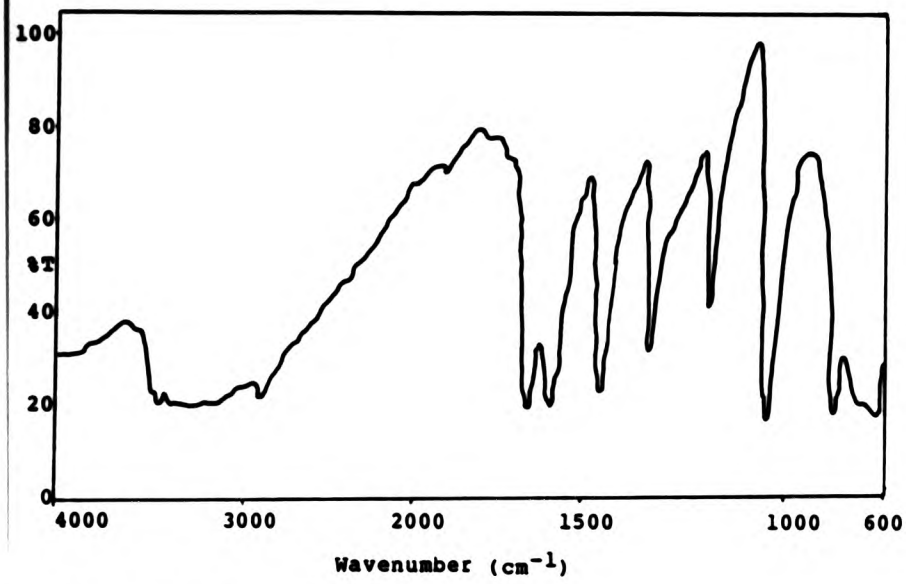


Figure 1.1 I.r. Spectrum of $DagH_2$

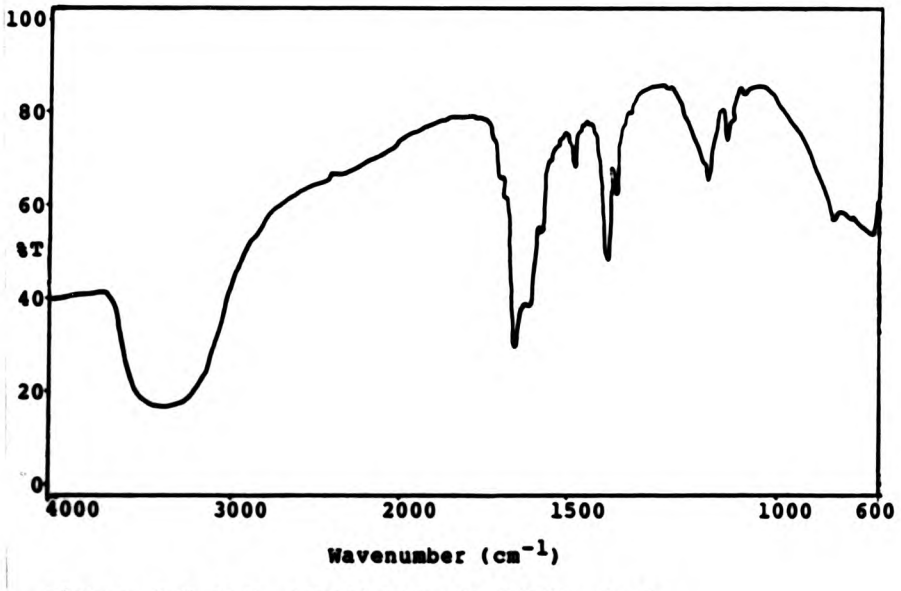


Figure 1.2 I.r. Spectrum of $NiCl_2.dagH_2$

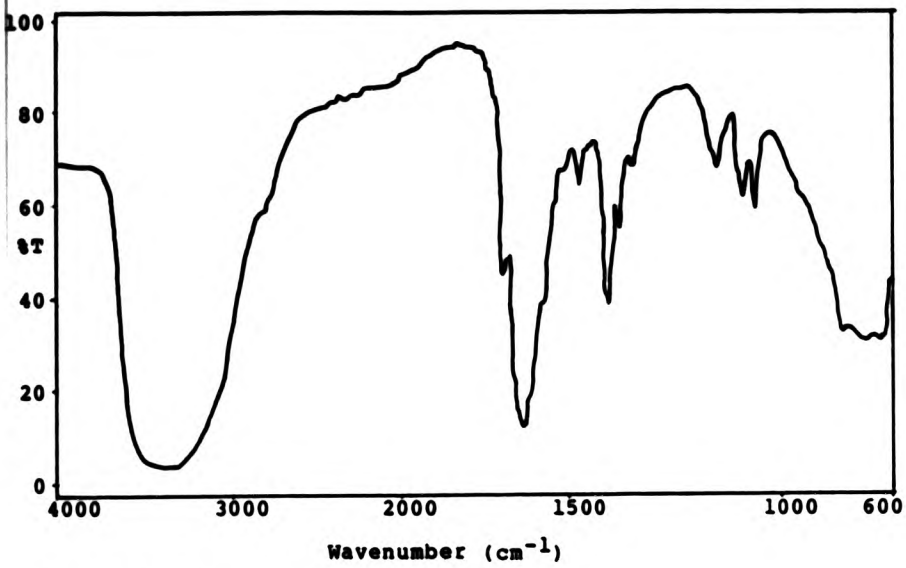


Figure 1.3 I.r. Spectrum of $NiCl_2.2dagH_2$

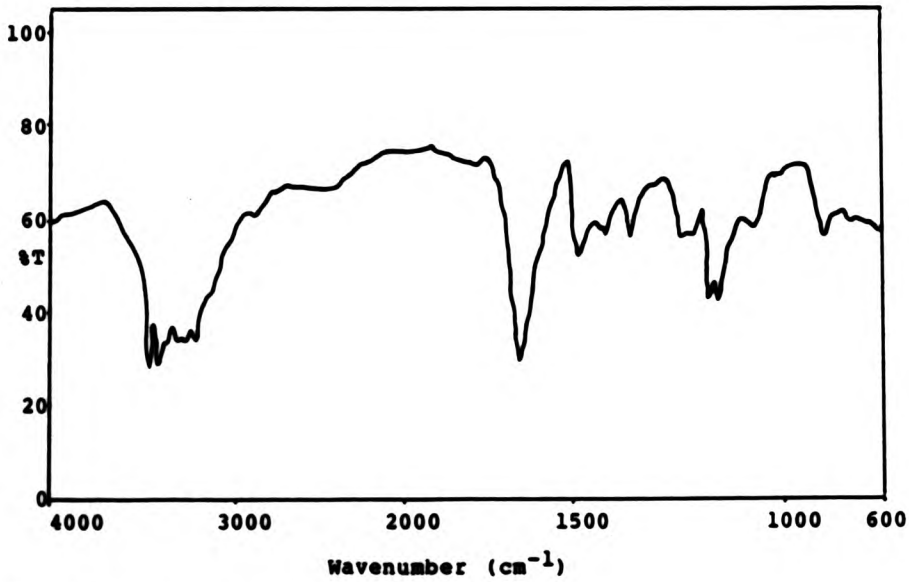
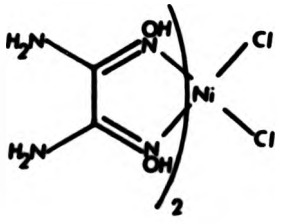


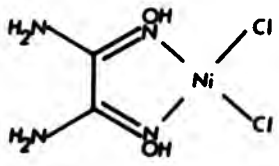
Figure 1.4 I.r. Spectrum of $Ni(dagH)_2$

The magnetic moment of the $NiCl_2.dagH_2$ is 3.01 μ_B, which is consistent with a distorted tetrahedral structure.[59] The molar conductivity of the 1:1 adduct in methanol is 173 ohm^{-1} cm^2 mol^{-1}, which is within the expected region for a 2:1 electrolyte (115 - 250 ohm^{-1} cm^2 mol^{-1}).[44] Its u.v./visible spectrum shows absorption maxima at 203 nm (ϵ_{max}= 741 m^2 mol^{-1}), 227 nm (ϵ_{max}= 353 m^2 mol^{-1}), 346 nm (ϵ_{max}= 142 m^2 mol^{-1}), 386 nm (sh.), and 620 nm (ϵ_{max}= 52 m^2 mol^{-1}). The latter band is due to the transition from the $^3T_1(F)$ ground state to the $^3T_1(P)$ state, typical of nickel(II) complexes with such a configuration.[59]

The magnetic moment of $NiCl_2.2dagH_2$ is 3.36 μ_B, and is indicative of octahedral geometry.[59] Furthermore, in solution, the octahedral configuration of this complex is also evident from its electronic spectrum. This exhibits absorption maxima at 208 nm (ϵ_{max}= 906 m^2 mol^{-1}), 233 nm (ϵ_{max}= 431 m^2 mol^{-1}), 344 nm (ϵ_{max}= 200 m^2 mol^{-1}), and a band at 577 nm (ϵ_{max}= 74 m^2 mol^{-1}) due to the transition from $^3A_{2g}$ to $^3T_{1g}(F)$.[59] This complex has a molar conductivity of <10 ohm^{-1} cm^2 mol^{-1} in methanol, thus suggesting that it is a non-electrolyte.



1.19



1.20

1.4 The X-ray Crystallographic Study of Bis(diaminoglyoxime)-nickel(II) Chloride

The adduct bis(diaminoglyoxime)nickel(II) chloride, $NiCl_2.2dagH_2$ was intuitivelly described in the past as having a structure of type I (Scheme 1.3).[51] However, the present X-ray crystallographic study has shown that the structure acquired by $NiCl_2.2dagH_2$ is not of type I, but of type II.

The synthesis of bis(diaminoglyoxime)nickel(II) chloride was accomplished by the 2:1 reaction of diaminoglyoxime and nickel(II) chloride in aqueous methanol at 65 ^{o}C. The pH was adjusted to ca. 2 with the dropwise addition of dilute hydrochloric acid. The product was crystallised by slow evaporation from methanol:water.

The compound forms plate-like crystals in the monoclinic space group $P2_1/c$. The unit cell dimensions were found to be:

a= 14.327 (3), b= 14.109 (3), c= 6.638 (2) Å, β = 111.06 (2)^{o}.
V= 1341.80 Å^3.
Z= 4.
d_c= 1.81 g cm^{-3}.

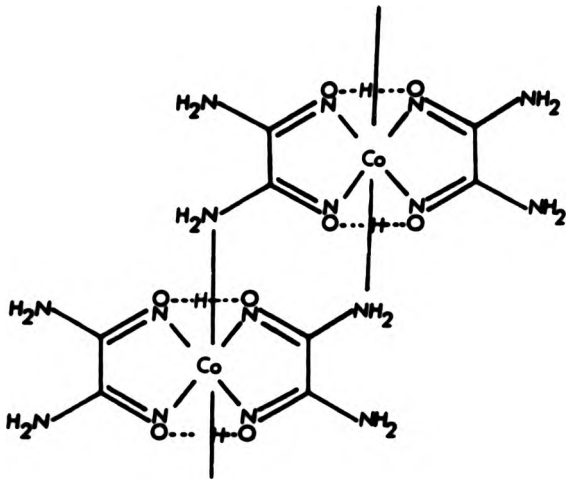
A crystal of approximate dimensions 0.24 x 0.08 x 0.24 mm was used for the investigation. All X-ray measurements were made with Mo Kα radiation, and a scan width of 0.86^{o}, using a Philips PW 1100 four-circle diffractometer. A total of 1815 reflections were collected, of which 1770 were subsequently

used in the refinement ($I/\sigma(I)>3.0$). The structure was solved by the Patterson method, and the final R and R_w refinement values converged to 0.0541 and 0.0573, respectively.

A perspective view of the adduct bis(diaminoglyoxime)-nickel(II) chloride is shown in Figure 1.5. The fractional atomic coordinates and thermal parameters of the non-hydrogen atoms are shown in Table 1.3, and the fractional atomic coordinates for the hydrogen atoms are shown in Table 1.4. The bond lengths and angles within the complex molecule are given in Tables 1.5 and 1.6, respectively. Other data of this study are included in the Appendix.

The nickel atom in bis(diaminoglyoxime)nickel(II) is in an approximately octahedral arrangement with two neutral anti-diaminoglyoxime ligands and two chlorine atoms. The two chlorine atoms are bonded to the nickel atom in a cis fashion. The dioxime ligands coordinate through the oximic nitrogens to give planar five-membered rings. The amino groups in this complex, which are also in plane with the chelated rings are not involved in any coordination with the nickel atom. This is in contrast to the previously reported crystal structure of bis(diaminoglyoximato)cobalt(II)-(diaminoglyoxime), in which the amino nitrogen atoms participate in intermolecular bonding with the cobalt atom.[53] In this cobalt(II) complex, only the two anionic $dagH^-$ ligands are bonded to the metal atom, whilst the neutral $dagH_2$ is a lattice species. Each of the bonded ligands chelates to the metal via its oximic nitrogens to give planar

five-membered rings and units of the type $Co(dagH)_2$. These units are linked together via the amino groups of adjacent units to give a chain polymeric structure (1.21).



1.21

The relatively short O1-Cl2 distance (3.11 Å) in $NiCl_2.2dagH_2$ indicates the presence of O-H-Cl hydrogen bridge (Appendix). This is comparable to the structure of (dimethylglyoxime)copper(II) chloride, $CuCl_2.dmgH_2$, in which hydrogen bonding of this type was indicated by a distance of 3.03 Å between an oxime oxygen and a chlorine.[28] The average Ni-N distance in $NiCl_2.2dagH_2$ is 2.06 Å, and is slightly longer than the Ni-N distance in other nickel(II) oximic complexes. For example, in bis(diaminoglyoximato)nickel(II) dihydrate,[56] and in bis(diaminoglyoximato)nickel(II)-water-

dimethylformamide,[55] the average Ni-N distance is 1.86 Å (Table 1.7). The long Ni-N distances in $NiCl_2.2dagH_2$ suggest that these bonds are weaker than the Ni-N bonds in $Ni(dagH)_2.2H_2O$ and $Ni(dagH)_2.H_2O.DMF$. The average N-O distance in $NiCl_2.2dagH_2$ is 1.41 Å, and this is similar to the N-O distance in complexes of diaminoglyoxime,[53-56] as well as the corresponding distance in free glyoxime (1.40 Å).[18] However, this is significantly longer than the N-O distance in $Ni(dmgH)_2$ (1.35 Å),[24] and $Cu_2(dmgH)_4$ (1.33 Å).[26] The average C=N bond length in $NiCl_2.2dagH_2$ is 1.30 Å, and this is similar to the C=N bond distance in all the complexes of diaminoglyoxime shown in Table 1.7. However, the C=N bond length in the adduct is longer than the C=N bond distance in free glyoxime (1.28 Å).[17] The C-C bond distance in the adduct $NiCl_2.2dagH_2$ (1.49 Å) is similar to that found in the other complexes of diaminoglyoxime.[53-56]

The two N - Ni - N angles in the chelate [N(2) - Ni - N(1)= 76.1°, N(4) - Ni - N(3)= 75.9°] are considerably smaller than the N - M - N bond angle in most complexes of dioximes, which is 80° ± 2°, and is independent of metal and residual bonds.[8] Although the octahedral arrangement around the nickel atom in $NiCl_2.2dagH_2$ is expected to decrease this angle, other factors must also contribute to this. Intramolecular hydrogen bonding, involving O-H-Cl bridges is likely to affect the size of this angle. Hydrogen bonding of this type was found to be present in the structure of $CuCl_2.dmgH_2$, in which the N - Cu - N angle is 77.0°.[28] On the other hand, in the

octahedral complex $CoCl_3.3dagH_2$, which also involves hydrogen bonding of this type, the mean bond angle N - Co - N in the chelate ring is 80°, and does not deviate from the normal N - M - N angle found in most metal complexes of dioxime.[54] The low value of the N - Ni - N angle in $NiCl_2.2dagH_2$ compared to other dioxime complexes, is also a result of the increase in the Ni-N bond distance in this complex. As indicated in Table 1.7, an increase in the M-N distance among complexes of dioximes, generally leads to a decrease in the N - M - N angle.

Table 1.3 Fractional Atomic Coordinates and Thermal Parameters ($Å^2$) of the non-Hydrogen Atoms

Atom	x	y	z	U_{iso} or U_{eq}
Ni	0.1637(9)	0.1356(4)	0.2434(4)	0.0191(3)
Cl(1)	-0.2302(19)	0.1118(9)	0.1664(8)	0.0274(6)
Cl(2)	0.1261(21)	0.3094(9)	0.2507(9)	0.0324(7)
O(1)	0.1626(6)	0.2357(2)	0.0527(2)	0.037(2)
O(2)	0.2828(6)	-0.0815(2)	0.2664(2)	0.028(2)
O(3)	-0.0190(6)	0.0404(3)	0.3870(2)	0.039(2)
O(4)	0.6451(6)	0.2128(2)	0.3348(2)	0.033(2)
N(1)	0.2059(6)	0.1537(3)	0.1113(3)	0.022(1)
N(2)	0.2285(6)	0.0004(2)	0.2055(3)	0.018(1)
N(3)	0.1456(6)	0.0972(3)	0.3756(3)	0.024(1)
N(4)	0.4805(6)	0.1550(2)	0.3467(3)	0.021(1)
N(11)	0.2368(7)	0.0793(3)	-0.0301(3)	0.029(2)
N(21)	0.3427(7)	-0.0865(3)	0.0942(3)	0.035(2)
N(31)	0.3352(7)	0.0671(3)	0.5455(3)	0.029(2)
N(41)	0.6544(8)	0.1930(3)	0.5167(3)	0.038(3)
C(1)	-0.2345(7)	0.0798(3)	0.0640(3)	0.018(1)
C(2)	0.2733(7)	-0.0081(3)	0.1258(3)	0.018(1)
C(3)	0.3138(7)	0.1033(3)	0.4558(3)	0.020(1)
C(4)	0.4951(7)	0.1545(3)	0.4396(3)	0.021(1)

Table 1.4 Fractional Atomic Coordinates for the Hydrogen Atoms

Atom	x	y	z
H(1)	0.1910	0.2800	0.1030
H(2)	0.3110	-0.1310	0.2540
H(3)	0.8600	0.0340	0.3170
H(4)	0.6480	0.1820	0.2710
H(11a)	0.2160	0.0180	-0.0580
H(11b)	0.2010	0.1310	-0.0660
H(21a)	0.3660	-0.1410	0.1340
H(21b)	0.3721	-0.0875	0.0248
H(31a)	0.4820	0.0650	0.5960
H(31b)	0.2260	0.0340	0.5460
H(41a)	0.7490	0.2350	0.4970
H(41b)	0.6781	0.1781	0.5939

Table 1.5 Bond lengths (Å)

Ni	-Cl(1)	2.469(1)
Ni	-Cl(2)	2.471(1)
Ni	-N(1)	2.027(4)
Ni	-N(2)	2.074(4)
Ni	-N(3)	2.014(4)
Ni	-N(4)	2.109(3)
O(1)	-N(1)	1.398(5)
O(2)	-N(4)	1.413(5)
O(3)	-N(3)	1.412(6)
O(4)	-N(4)	1.422(6)
N(1)	-C(1)	1.293(6)
N(2)	-C(2)	1.285(7)
N(3)	-C(3)	1.286(5)
N(4)	-C(4)	1.300(6)
N(11)	-C(1)	1.354(6)
N(21)	-C(2)	1.338(6)
N(31)	-C(3)	1.342(6)
N(41)	-C(4)	1.339(6)
C(1)	-C(2)	1.491(6)
C(3)	-C(4)	1.491(7)

Table 1.6 Bond Angles (°)

Cl(2)	-Ni	-Cl(1)	92.7(1)	N(21)	-C(2)	-N(2)	126.5(4)
O(1)	-N(1)	-Ni	126.7(3)	N(31)	-C(3)	-N(3)	126.1(5)
O(2)	-N(2)	-Ni	128.4(3)	N(41)	-C(4)	-N(41)	120.7(5)
O(3)	-N(3)	-Ni	124.9(2)	C(1)	-N(1)	-Ni	118.9(3)
O(4)	-N(4)	-Ni	127.3(2)	C(1)	-N(1)	-O(1)	113.0(4)
N(1)	-Ni	-Cl(1)	94.6(1)	C(1)	-C(2)	-N(2)	113.8(4)
N(1)	-Ni	-Cl(2)	88.0(1)	C(1)	-C(2)	-N(21)	119.6(4)
N(2)	-Ni	-Cl(1)	92.5(1)	C(2)	-N(2)	-Ni	117.1(3)
N(2)	-Ni	-Cl(2)	163.6(1)	C(2)	-N(2)	-O(2)	112.6(4)
N(2)	-Ni	-N(1)	76.1(2)	C(2)	-C(1)	-N(1)	112.7(4)
N(3)	-Ni	-Cl(1)	88.4(1)	C(2)	-C(1)	-N(11)	121.7(4)
N(3)	-Ni	-Cl(2)	100.7(1)	C(3)	-N(3)	-Ni	119.8(4)
N(3)	-Ni	-N(1)	170.7(2)	C(3)	-N(3)	-O(3)	113.2(4)
N(3)	-Ni	-N(2)	95.0(2)	C(3)	-C(4)	-N(4)	113.2(4)
N(4)	-Ni	-Cl(1)	163.7(1)	C(3)	-C(4)	-N(41)	120.7(5)
N(4)	-Ni	-Cl(2)	86.1(1)	C(4)	-N(4)	-Ni	114.0(3)
N(4)	-Ni	-N(1)	101.6(2)	C(4)	-N(4)	-O(4)	110.4(3)
N(4)	-Ni	-N(2)	93.2(1)	C(4)	-C(3)	-N(3)	112.5(4)
N(4)	-Ni	-N(3)	75.9(2)	C(4)	-C(3)	-N(31)	121.3(4)
N(11)	-C(1)	-N(1)	125.6(4)				

Table 1.7 Bond Distance (Å) and Bond Angle (°) Data of Some Dioxime Complexes

Complex	M-N	N-O	C=N	C-C	O-O	N-M-N	Reference
$Co(dagH)_2.dagH_2$	1.88	1.37	1.29	1.48	2.61	82.3	53
$CoCl_3.3dagH_2$	1.91	1.39	1.30	1.48	2.85	79.8	54
$Ni(dagH)_2.H_2O.DMF$	1.86	1.36	1.31	1.47	2.49	83.1	55
$Ni(dagH)_2.2H_2O$	1.86	1.38	1.30	1.46	2.57	82.2	56
$CuCl_2.dmgH_2$	1.98	1.39	1.28	1.48	---	77.0	28

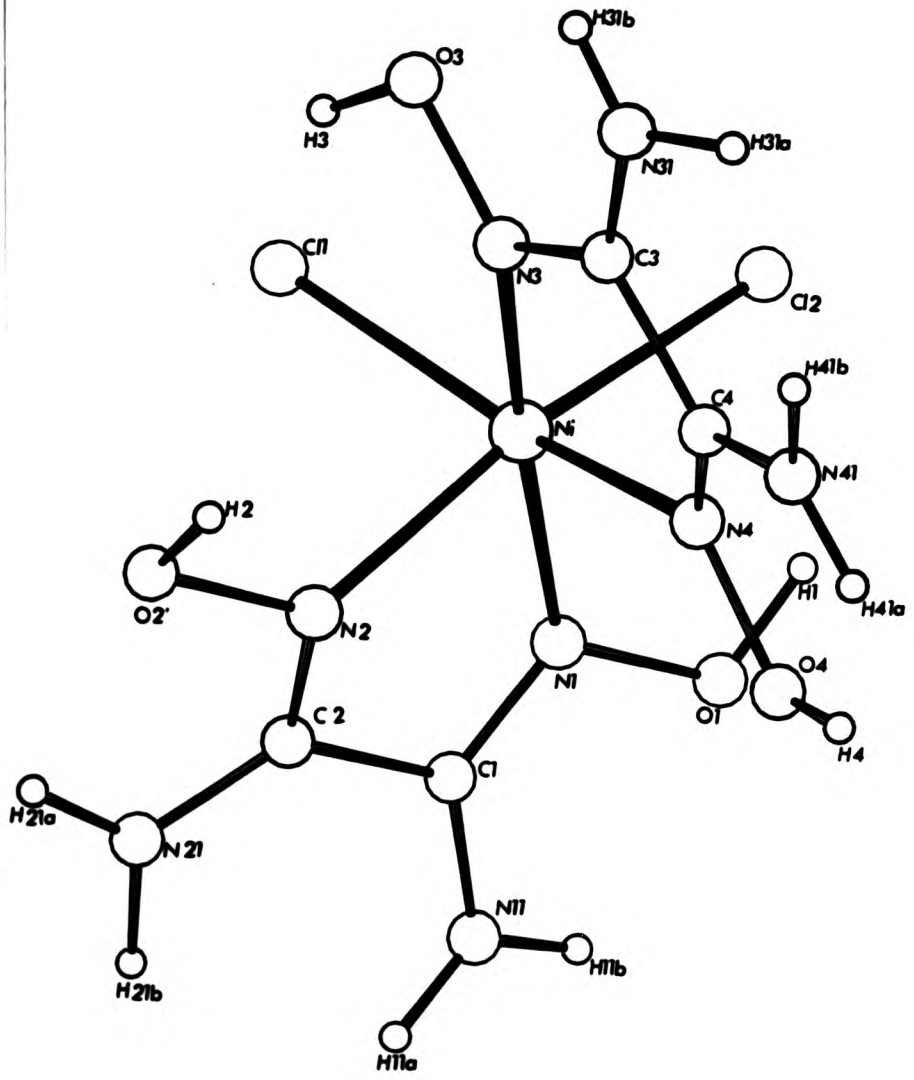


Figure 1.5 Structure of Bis(1,2-diaminoglyoxime)nickel(II) Chloride

1.5 References

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CHAPTER 2

2. Reactions of Dioximes with Reactive Substituents and of Their Complexes

2.1 Introduction

The reactive substituents in dichloroglyoxime, chloroglyoxime, diaminoglyoxime, and their complexes, may be utilised for the synthesis of a variety of compounds. Previously, such reactions received only limited attention.[1-5] In contrast, analogous reactions involving dioximes with alkyl or aryl substituents, and their complexes have attracted more attention.[6-11] During this work, a systematic study of the reactions of the following has been undertaken:

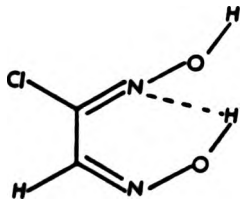
(a) dichloroglyoxime, anti-chloroglyoxime, and bis(chloroglyoximato)nickel(II) with compounds containing labile hydrogens

(b) diaminoglyoxime, bis(diaminoglyoximato)nickel(II), and bis(diaminoglyoximato)copper(II) monohydrate with compounds containing active halogens or carbonyl groups

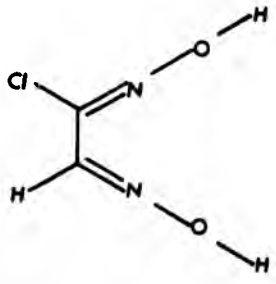
(c) diaminoglyoxime, bis(diaminoglyoximato)nickel(II), bis(diaminoglyoximato)copper(II) monohydrate, bis(diaminoglyoxime)nickel(II) chloride, and mono(diaminoglyoxime)nickel(II) chloride with dimethyl acetylenedicarboxylate.

2.2 Reactions of Dichloroglyoxime, and anti-Chloroglyoxime with Compounds Containing Labile Hydrogens

Chloroglyoxime exists in the three isomers syn, amphi, and anti.[12, 13] The amphi isomer of chloroglyoxime (2.1) rearranges to the anti form (2.2) in acidic media.[13, 14] The determination of the pH of aqueous solutions of these two isomers clearly shows that the anti form is a much stronger acid (pH 3.14) than the corresponding amphi form (pH 6.71).[15] Dissociation of H^+ ions in the amphi form is supressed by intramolecular hydrogen bonding, whereas the anti form is free from such interaction.[8]

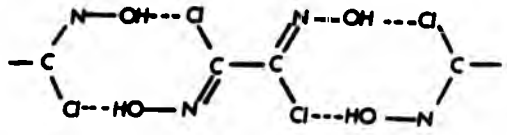


2.1



2.2

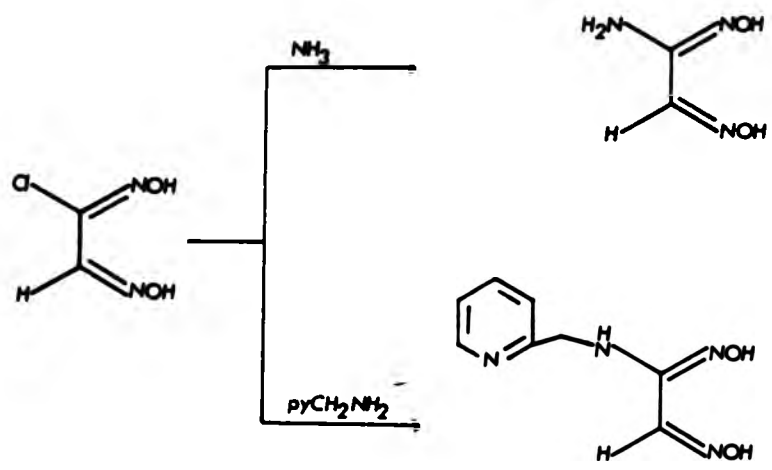
In the case of dichloroglyoxime, only the anti form has been isolated.[16, 17] A ^{36}Cl NQR study indicates that this form involves hydrogen bonding with s-trans configuration (2.3).[18]



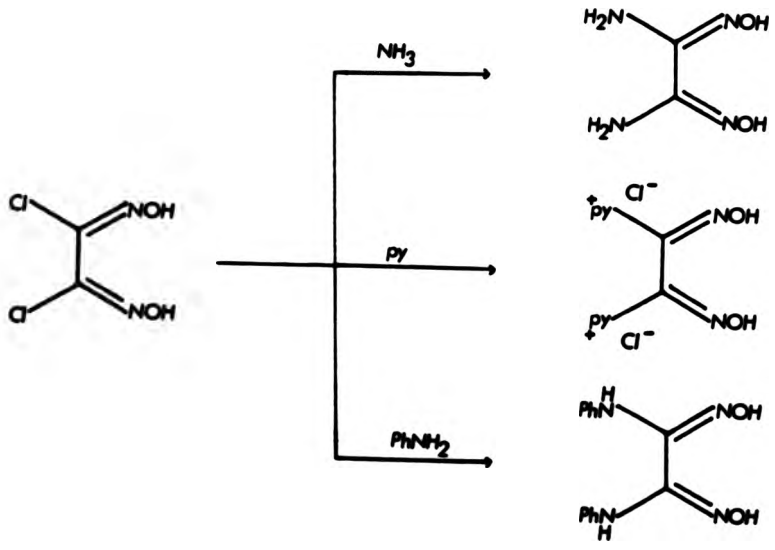
2.3

In chloroglyoxime and dichloroglyoxime, the chloro substituents are reactive due to activation of the C-Cl bond by the oximic group. Consequently, both chloroglyoxime, and dichloroglyoxime can react with compounds containing labile hydrogens via dehydrochlorination. Only a few such reactions have been reported.[5, 13, 19] The reactivity of the chloro-substituents in these compounds has also been demonstrated by their reactions with pyridine. In the case of dichloroglyoxime, reaction with excess pyridine leads to the formation of 1,2-dihydroxy-1,2-di(N-pyridinium) dichloride.[5] In the present study it was found that the anti isomer of chloroglyoxime reacts with pyridine to give 1,2-dihydroxyiminoethane-N-pyridinium chloride. As described in Chapter 1, these reactions involve a nucleophilic attack by the nitrogen of the amine on the oximic carbon. The reactions of anti-chloroglyoxime and dichloroglyoxime are illustrated in Schemes 2.1 and 2.2.

The oximic group of dichloroglyoxime is also reactive, and this has been demonstrated by its reaction with acetic anhydride which gives dichloroglyoxime diacetate.[14]



Scheme 2.1



Scheme 2.2

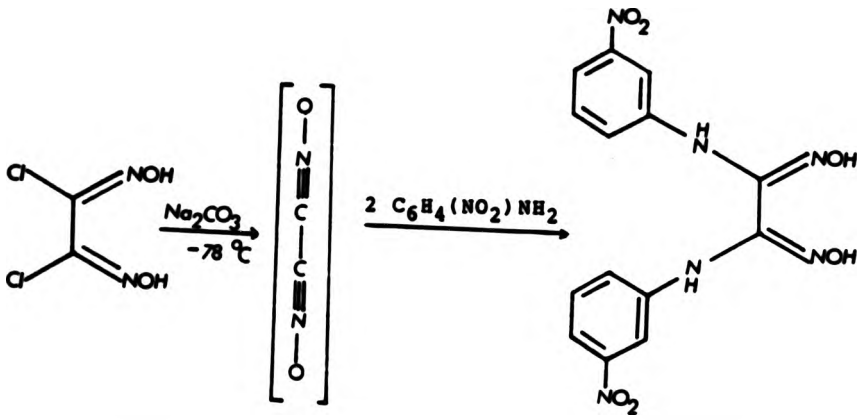
In this study, the behaviour of dichloroglyoxime with primary monofunctional and difunctional amines, as well as various of their derivatives, has been investigated. The systems examined involve 3-nitroaniline, ethylenediamine, piperazine, ethylene bisacetamide, and ethylene dinitramine. In addition, the previously reported preparation of 1,2-di(phenyl-N-amino)glyoxime from aniline and dichloroglyoxime has been confirmed.[5]

2.2.1 Reaction of Dichloroglyoxime with 3-Nitroaniline

Although dichloroglyoxime reacts smoothly with aniline, to give 1,2-di(phenyl-N-amino)glyoxime in moderate yield, it fails to react with 3-nitroaniline under similar conditions. In the case of 3-nitroaniline, this can be accounted in terms of the weaker basic character of the NH_2 group.[20] The 3-nitroanilino derivative (2.5) of dichloroglyoxime has been obtained through an alternative route. Previous studies showed that in aqueous sodium carbonate, dichloroglyoxime is converted to cyanogen di-N-oxide (2.4),[21] which is very reactive and has been used to synthesise several dioximes.[21, 22] This approach has also been effectively utilised in this study to synthesise 1,2-di(3-nitrophenyl-N-amino)glyoxime (Scheme 2.3).

The ^1H n.m.r. spectrum of 1,2-di(3-nitrophenyl-N-amino)-glyoxime shows two singlets at 11.2 and 8.2 ppm, and a multiplet at 7.2 - 7.7 ppm in the ratio 2:2:8. The signals at

11.2 and 8.2 ppm are due to OH and NH, respectively, as indicated by deuterium exchange. Further support for the formulation of this product is given by its EI and CI mass spectra (Chapter 3).



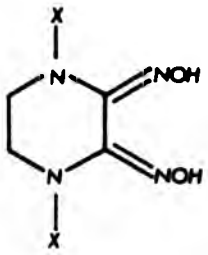
2.4 2.5

Scheme 2.3

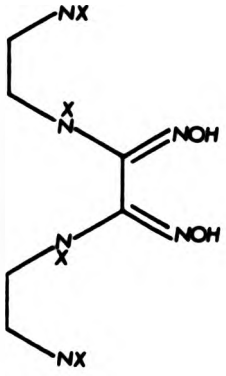
2.2.2 Reaction of Dichloroglyoxime with Diamino Compounds

The dehydrochlorination reaction of dichloroglyoxime with a difunctional amine of type $XHNCH_2CH_2NHX$ (X= e.g. H, OAc, NO_2) can, in principle, lead to three different types of compound (2.6 - 2.8). The nature of the product depends on the molar ratio of the reactants involved and the reaction conditions employed. A cyclic product (2.9), analogous to that shown in 2.6 has previously been obtained from the reaction of 1,2-bis(2-aminophenylamino)ethane with dichloroglyoxime in

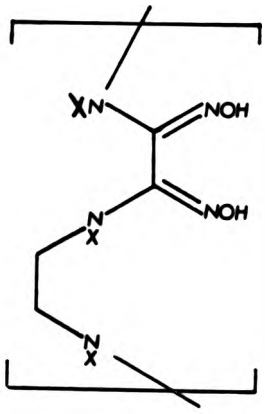
the presence of sodium hydrogen carbonate.[23] A polymeric product of type 2.8 has been obtained as the main product from the reaction of ethylenediamine and cyanogen-di-N-oxide.[21] During this study, compounds of types 2.7 and 2.8 have been obtained from reactions of dichloroglyoxime and difunctional amines.



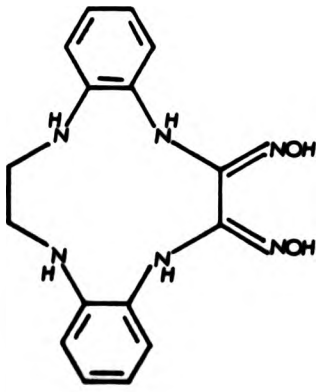
2.6



2.7



2.8

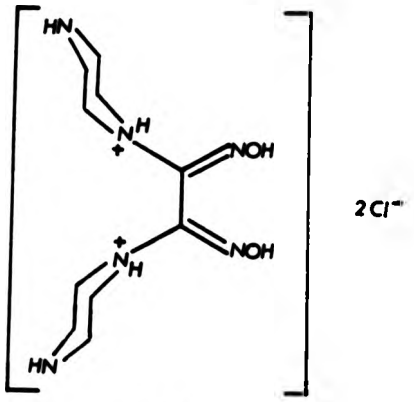


2.9

The reaction of dichloroglyoxime with ethylenediamine in 1:1 molar ratio led to the dihydrochloride salt of 2,3-dioximino-piperazine. Subsequent treatment of this compound with propylene oxide gave the free 2,3-dioximino-piperazine in high yield (2.6; X= H). This compound was previously isolated from the reaction of cyanogen di-N-oxide and ethylenediamine, but in a very low yield.[21] The monomeric nature of this compound is suggested by its high solubility in organic solvents, its relatively low melting point (201 - 202 ^{o}C), and is supported by its EI and CI mass spectra (Chapter 3). Its ^{1}H n.m.r spectrum shows a broad signal at 8.3 - 8.7 ppm and a singlet at 3.1 ppm in the ratio 1:1. The former exchanges with D_2O, and is assignable to the NOH and NH protons. The peak at 3.1 ppm is due to the methylene protons. The ^{13}C n.m.r spectrum of this compound shows two signals at 39 and 148 ppm. The latter is assignable to the CNOH carbons, because generally oximic carbons appear at 145 - 165 ppm,[24] and the signal at 39 ppm is thus assigned to the CH_2 carbons.

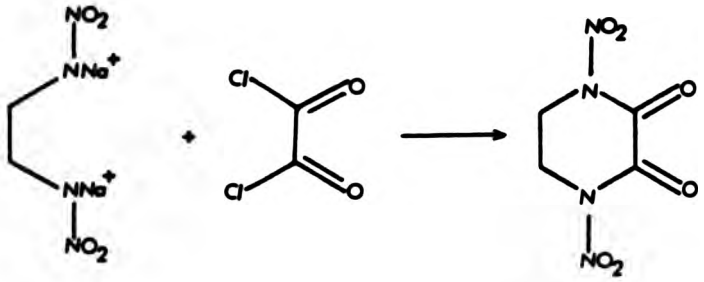
The reaction of dichloroglyoxime with piperazine did not lead to a cyclic product of type 2.6, even under high dilution conditions. Instead, reaction in 1:2 ratio occurred, and 1,2-dipiperazineglyoxime dihydrochloride (2.10) resulted. Such behaviour is in accord with the chair conformation of piperazine, which prevents cyclisation.[25] The formulation of 2.10 is indicated by its elemental analysis, and is supported by its ^{1}H n.m.r. spectrum in which the ratio of the methylene and oximic hydrogens is 8:1. The ^{13}C n.m.r. spectrum of this

compound provides further support for the proposed formulation, because it shows a signal at 169 ppm due to the oximic carbons, and a signal at 23 ppm due to the CH_2 carbons. In addition, in the i.r. spectrum of this compound, the appearance of the characteristic absorption of NH^+ at 2500 cm^{-1} provides evidence for salt formation.[26]

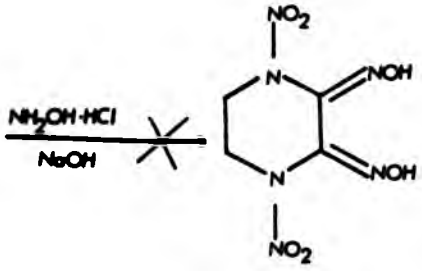


2.10

The reactions of dichloroglyoxime with ethylene bis-acetamide, and the sodium salt of ethylene dinitramine have been carried out with the expectation of synthesising compounds of type 2.6. However, in both cases no reaction occurred. The synthesis of 2.6 (X= NO_2) has also been attempted through the indirect route outlined in Scheme 2.4. The intermediate 2.11 was successfully obtained. However, subsequent treatment of this with hydroxylamine hydrochloride and sodium hydroxide failed to give the desired dioxime.



2.11

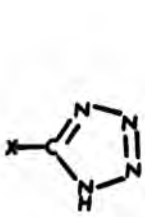


Scheme 2.4

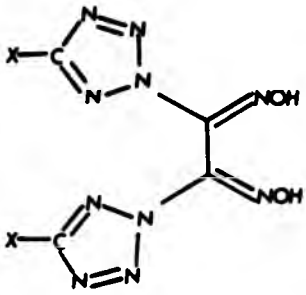
2.2.3 Reaction of Dichloroglyoxime and anti-Chloroglyoxime with 5C-Tetrazoles

In addition to their ability to undergo dehydrochlorination reactions with amines, dichloroglyoxime and chloroglyoxime are expected to react in an analogous fashion with other compounds containing labile hydrogens. 5C-substituted tetrazoles (2.12) contain a fairly reactive hydrogen, and their reactions with dichloroglyoxime and anti-chloroglyoxime

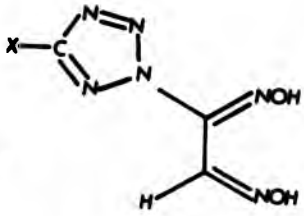
are expected to lead to tetrazolyl-substituted dioximes of types 2.13 and 2.14, respectively.



2.12



2.13



2.14

In the absence of any acid scavenger, neither dichloroglyoxime nor anti-chloroglyoxime reacted with tetrazole, 5-hydroxytetrazole, and 5-aminotetrazole. However, dichloroglyoxime reacted with the sodium salts of tetrazole, 5-chlorotetrazole, and 5-nitrotetrazole at -78 ^{o}C to give dioximes of type 2.13. The dioxime with the 5-nitrotetrazolyl substituents (2.13; X= NO_2) is unstable in the solid state, but its formation in solution was confirmed from a ^{1}H n.m.r. study (Tables 2.1). anti-Chloroglyoxime reacted with the sodium salts of tetrazole, and 5-chlorotetrazole to give products of type 2.14. These reactions also occurred at ambient temperature, but the yields of the products were much lower.

The tetrazolyl-substituted dioximes (2.13 and 2.14) have been characterised on the basis of their elemental analyses, i.r., mass, ^{1}H n.m.r, and ^{13}C n.m.r spectra. The i.r. spectra of

these compounds include broad bands at 3200 - 3400 cm^{-1}, which are indicative of hydrogen-bonding, a typical feature of vic-dioximes.[15, 27] Also present are intense bands in the region of 1320 cm^{-1}, which are assignable to the cyclic group N-N=N.[28] Their isobutane PICI and methane NICI mass spectra support the formulations of these dioximes (Chapter 3). The ^{1}H and ^{13}C n.m.r. data and appropriate assignments are presented in Tables 2.1 and 2.2.

The dioximes with the 5-chlorotetrazolato substituents, 1,2-di(5-chlorotetrazolato)glyoxime (2.13; X= Cl), and 1-(5-chlorotetrazolato)glyoxime (2.14; X= Cl) show the most deshielded oximic protons (14.1 and 12.4 ppm, respectively). This is probably due to intramolecular hydrogen bonding involving the chlorine atoms of the tetrazolyl substituents and the hydrogen atoms of the oximic groups. Intramolecular and intermolecular hydrogen bonding is a well-known factor responsible for the low-field chemical shift of hydroxyl protons.[29, 30] In view of this phenomenon, the chemical shift of the oximic hydrogen influenced by intramolecular H-Cl bonds was studied by examining the ^{1}H n.m.r. spectrum of dichloroglyoxime at different temperatures (Section 2.2.4).

The ^{13}C n.m.r. spectrum of 1,2-di(5-chlorotetrazolato)-glyoxime (2.13; X= Cl) shows four different signals at 136.4, 157.3, 161.3, and 172.3 ppm. This suggests that the tetrazolato carbons are in different environments, giving rise to the signals at 136.4, and 157.3 ppm. Similarly, the non-equivalent oximic carbons give rise to the two signals

at 161.3, and 172.3 ppm. This is probably due to intramolecular interactions between the chlorine atoms of the tetrazolato units with the hydrogen atoms of oxime groups.

Table 2.1 Chemical Shifts in the ^{1}H n.m.r. of the Tetrazolyl-substituted Dioximes in DMSO d_6

	δ (ppm)			
Compound	NOH	NOH	C-H (dioxime)	C-H (tetrazole)
2.13; X= H	11.7	11.7	---	9.8
2.13; X= Cl	14.1	14.1	---	---
2.13; X= NO_2	13.0	13.0	---	---
2.14; X= H	12.4	11.5	8.1	9.5
2.14; X= Cl	12.3	11.1	8.2	---

Table 2.2 Chemical Shifts in the ^{13}C n.m.r. of the Tetrazolyl-substituted Dioximes in DMSO d_6

	δ (ppm)		
Compound	C (dioxime)	C (dioxime)	C (tetrazole)
2.13; X= H	168.3	168.3	144.4
2.13; X= Cl	172.3	161.3	157.3/136.4
2.14; X= H	153.7	144.6	137.8
2.14; X= Cl	141.8	137.0	136.5

2.2.4 Hydrogen Bonding in Dioximes Studied by ^1H n.m.r.

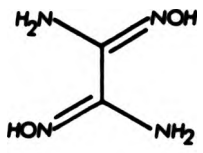
During this study, the effect of intramolecular hydrogen bonding on the chemical shifts of oximic protons in dioximes has been investigated. In the ^1H n.m.r. spectra of dichloroglyoxime, anti-chloroglyoxime, and diaminoglyoxime, at ambient temperature (303 K), the oximic proton signals appear at 12.0, 12.7 and 12.2, and 9.7 ppm, respectively. Although intermolecular hydrogen bonding is involved in all three dioximes, intramolecular hydrogen bonding between the chlorine atoms and the hydrogen atoms of the oxime groups in dichloroglyoxime and anti-chloroglyoxime cause a low-field shift of the oxime protons. Furthermore, an increase in temperature, causes a high-field chemical shift of the oximic proton in dichloroglyoxime to 11.8 ppm, due to the breaking of the intramolecular H-Cl bonds (Table 2.3).

Table 2.3 The Effect of Temperature on the Chemical Shift of the Oximic Group of Dichloroglyoxime

Temperature (K)	δ(ppm)
303	12.6
308	11.9
318	11.8
323	11.8

2.3 Reaction of Diaminoglyoxime and of its Copper(II) and Nickel(II) Complexes

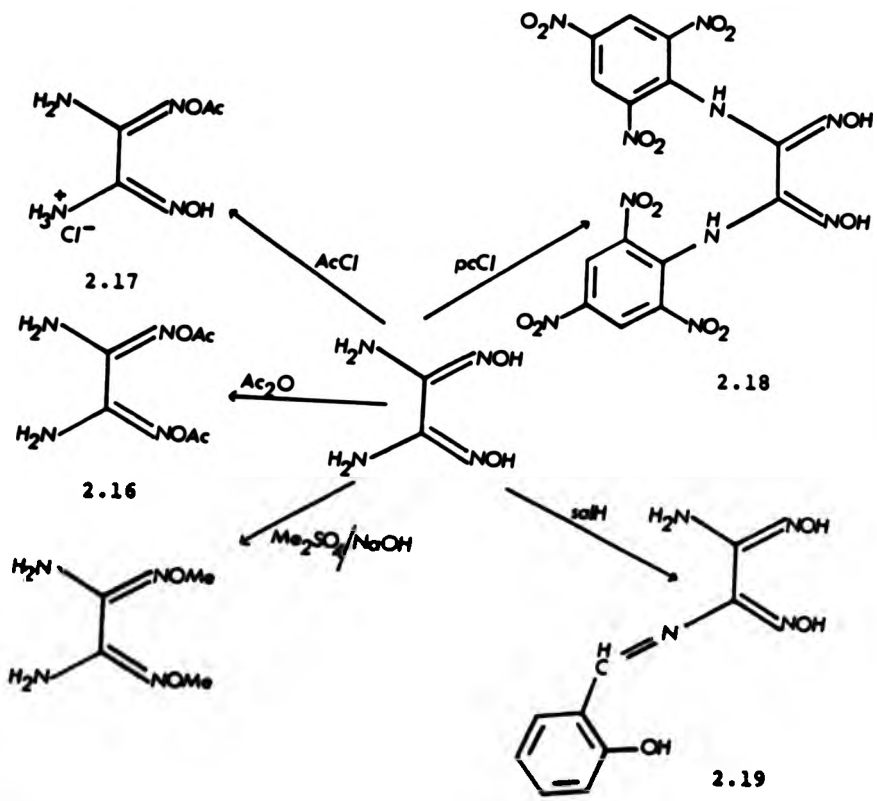
In recent years there has been considerable interest in the chemistry of diaminoglyoxime.[2, 5, 31-34] In solution, diaminoglyoxime has the oximic groups anti to the amino groups, and involves hydrogen bonding with s-trans configuration (2.15). This property is indicated by its ultraviolet spectrum which is similar to that of glyoxime and dimethylglyoxime.[15, 32]



2.15

Diaminoglyoxime has a potentially rich organic chemistry as it can function both as a dioxime and an amino compound (Scheme 2.5). Diaminoglyoxime reacts with acetic anhydride in an analogous fashion to dichloroglyoxime, to give diaminoglyoxime O-diacetate (2.16).[2] However, with acetyl chloride it gives the hydrochloride salt of the corresponding O-monoacetate derivative (2.17).[5] Both these reactions involve reaction at the oximic site of the dioxime. Other reactions may also occur at the oximic site of

diaminoglyoxime, such as the reaction with methyl sulphate in the presence of sodium hydroxide which gives an oxime ether.[35] A recent study shows that diaminoglyoxime reacts at the amino site with 2,4,6-trinitrochlorobenzene (picryl chloride) via dehydrochlorination to give 1,2-di-(2,4,6-trinitrophenyl-N-amino)glyoxime (2.18).[5] The same study reports a condensation reaction involving diaminoglyoxime and salicyladehyde which gives 1-amino-2-(2-hydroxybenzyl-N-imino)glyoxime (2.19).[5]



Scheme 2.5

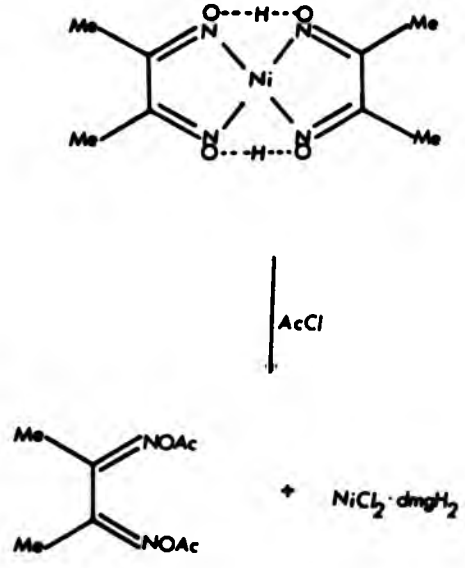
During the present studies, reactions of diaminoglyoxime and its copper(II) and nickel(II) complexes with nitro-substituted chlorobenzenes, acetylating reagents, carbonyl compounds, and dimethyl acetylenedicarboxylate, as well as reactions with boron trifluoride have been investigated.

2.3.1 Reaction with Acetylating Reagents

As discussed above, diaminoglyoxime reacts with acetic anhydride at the oxime site to give the O-diacetate derivative (2.16).[2] Reaction of the dioxime with acetyl chloride results in the formation of the hydrochloride salt of the O-monoacetate derivative of diaminoglyoxime (2.17), and trace quantities of the N-acetylated dioxime.[5] The reaction of diaminoglyoximato complexes with acetyl chloride was not previously studied.

During this study, it was found that when bis(diaminoglyoximato)nickel(II) was mixed with acetyl chloride in 1:4 molar ratio, no reaction occurred. This is in contrast with analogous reactions involving the nickel(II), palladium(II), and platinum(II) complexes of dimethylglyoxime, which react with acetyl chloride to give the free O-acetylated ligand and the corresponding 1:1 metal(II) chloride: dimethylglyoxime adduct (Scheme 2.6).[9] However, bis(diaminoglyoximato)nickel(II) reacts with excess acetyl chloride, to give a nickel-containing product of ill-defined i.r. spectrum, and a mixture of organic products which could

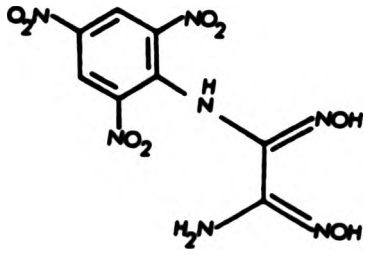
not be separated. Acetylation of this nickel(II) complex of diaminoglyoxime was also attempted using acetic anhydride. Under anhydrous conditions, the complex failed to react with acetic anhydride, whereas in the presence of atmospheric moisture it reacted to give diaminoglyoxime O-diacetate and nickel(II) acetate. This may be due to hydrolysis of the anhydride to give acetic acid, which then reacts with the bis(diaminoglyoximato)nickel(II) to give nickel(II) acetate and diaminoglyoxime. Subsequent acetylation of the latter gives the corresponding O-diacetate.



Scheme 2.6

2.3.2 Reaction with Nitro-substituted Chlorobenzenes

Re-examination of the reaction between 2,4,6-trinitrochlorobenzene with diaminoglyoxime in 1:2 molar ratio confirms that it gives 1,2-di(2,4,6-trinitrophenyl-N-amino)-glyoxime (2.18) as reported earlier.[5] In addition, it has now been shown that this reaction also leads to the formation of some 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime (2.20). This monosubstituted product has also be obtained from the 1:1 reaction of 2,4,6-trinitrochlorobenzene and diaminoglyoxime. A monosubstituted product, 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (2.21), also resulted from the reaction of the dioxime and 2,4-dinitrochlorobenzene, but in this case prolonged heating was required. In contrast, all three isomeric mononitrochlorobenzenes did not react with diaminoglyoxime even under forcing conditions. These observations clearly reflect the relative reactivity of the C-Cl bond in the nitrochlorobenzenes.[36]



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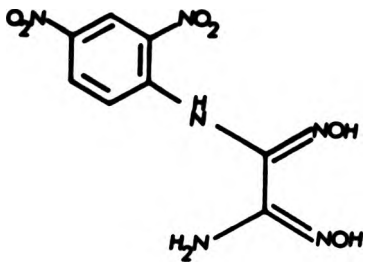


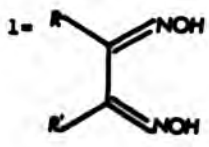
2.21

Diaminoglyoxime reacts with the chloronitrobenzenes, via dehydrochlorination, and the nitrobenzene cation, stabilised by the nitro groups, attacks the amino group. This type of behaviour is in contrast to the reaction of diaminoglyoxime with acetyl chloride, which involves attack on the oximic site (Scheme 2.5).[5]

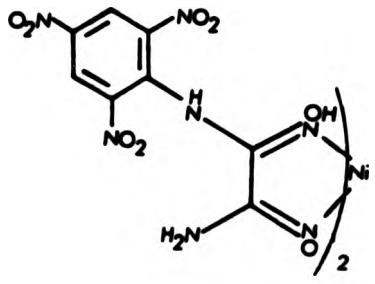
The involvement of the amino rather than the oximic group of the dioxime in these reactions is indicated by the readiness of the products to form complexes with various metal ions (Section 2.5, and 2.6). Furthermore, their ^{1}H n.m.r. spectra show signals indicative of oximic compounds (Table 2.4). Attack on the amino group also occurs when the copper(II) and nickel(II) complexes of diaminoglyoxime react with 2,4,6-trinitrochlorobenzene.

Table 2.4 ^{1}H n.m.r. Data of the Dioximes with Nitro-aromatic Substituents

Dioxime[1]		^{1}H n.m.r data		
R	R'	δ(ppm)	Ratio	Group
$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	8.4/7.9	4	CH(ar.)
		10.0	2	NH
		10.2	2	NOH
$C_6H_2(NO_2)_3NH$	NH_2	5.9	2	NH_2
		8.4/7.8	2	CH(ar.)
		9.6	1	NH
		11.0-11.2	2	NOH
$C_6H_3(NO_2)_2NH$	NH_2	5.7	2	NH_2
		8.6-7.7	3	CH(ar.)
		9.8	1	NH
		10.4	1	NOH
		10.9	1	NOH

1= 

It has been reported that bis(diaminoglyoximato)nickel(II) reacts at 65 °C with 2,4,6-trinitrochlorobenzene to give bis(1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoximato)-nickel(II) (2.22) in low yield.[5] This reaction was reinvestigated during this work. The findings confirmed the formation of this complex, and showed that the reaction also occurs at ambient temperature. In addition, it was found that at either temperature, the reaction led to the formation of the adduct mono(diaminoglyoxime)nickel(II) chloride (c.f., Chapter 1, 1.20) and free 1-amino-2-(2,4,6-trinitro-phenyl-N-amino)glyoxime (2.20). The formation of these compounds is due to the reaction between bis(diaminoglyoximato)nickel(II) or bis(1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoximato)-nickel(II) and hydrogen chloride which accompanies the formation of the latter.

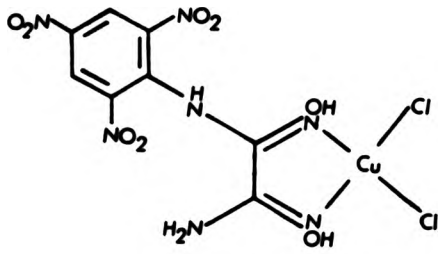


2.22

Significantly, when the reaction between bis(diamino-glyoximato)nickel(II) and 2,4,6-trinitrochlorobenzene was

carried out in the presence of the acid scavenger sodium hydrogen carbonate, the yield of bis(1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoximato)nickel(II) increased.

In contrast to the $Ni(dagH)_2$/picryl chloride system, bis(diaminoglyoximato)copper(II) monohydrate reacted with picryl chloride at 65 ^{o}C to give only the 1:1 adduct (1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime)copper(II) chloride (2.23). At ambient temperature, no reaction occurred.



2.23

Neither the copper(II) nor the nickel(II) bisdiaminoglyoximate reacted with 1-chloro-2,4-dinitrobenzene or 1-chloro-2-nitrobenzene. This can be related to the relative reactivity of the C-Cl bond in nitro-substituted chlorobenzenes which increases with additional nitro groups.[36]

The magnetic moment of the complex obtained from the $Cu(dagH)_2.H_2O$/picryl chloride (2.23) system is 1.13 μ_B,

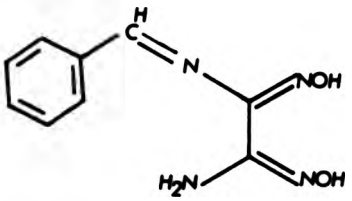
which is significantly lower than that expected for a magnetically dilute copper(II) species (1.75 - 2.20 μ_B).[37] This suggests that some association between neighbouring molecules may occur. Such association was noted for the analogous compound (dimethylglyoxime)copper(II) chloride, which was shown to be dimeric in the solid state.[38]

The electronic spectrum of the complex (1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime)copper(II) chloride (2.23) consists of absorption maxima at 353 nm (ϵ_{max} = 21 m^2 mol^{-1}), 395 nm (ϵ_{max} = 18 m^2 mol^{-1}), 540 nm (sh.), and 653 nm (sh.), which is similar to copper(II) complexes with a distorted octahedral structure.[39, 40] In methanolic solution, this complex dissociates as indicated by a molar conductivity of 237 ohm^{-1} cm^2 mol^{-1}, which suggests that this is a 2:1 electrolyte.[41]

2.3.3 Reaction with Carbonyl Compounds

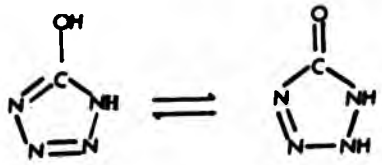
Previously, it was reported that salicylaldehyde reacts with diaminoglyoxime to give 1-amino-2-(hydroxybenzyl-N-imino)glyoxime (2.19).[5] In the present study, it has been shown that benzaldehyde reacts with the dioxime in 1:2 molar ratio in an analogous fashion to give the monosubstituted product 1-amino-2-(benzyl-N-imino)glyoxime (2.24). The ^1H n.m.r. spectrum of this dioxime shows signals in the expected ratio at 10.0 and 9.8 ppm due to the oximic

protons, 7.4-7.8 ppm due to the aromatic protons, 5.8 ppm due to to the exocyclic methine proton, and 5.2 ppm due to the amino protons. In contrast to the free diaminoglyoxime, the copper(II) and nickel(II) complexes of the dioxime fail to react with benzaldehyde.

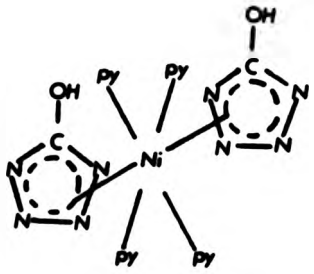


2.24

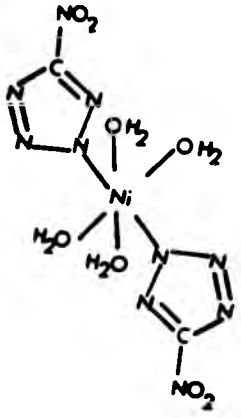
Tetrazolone, which exhibits tautomeric behaviour (Scheme 2.7),[42, 43] failed to react with diaminoglyoxime, but reacted with bis(diaminoglyoximato)nickel(II) in pyridine. However, the reaction does not involve condensation of the amino group and carbonyl group, but ligand exchange occurs to give tetrapyridine(5-hydroxytetrazolato)nickel(II) (2.25). Ligand exchange also occurs in the reaction of sodium 5-nitrotetrazolate with bis(diaminoglyoximato)nickel(II) in aqueous medium. In this case, the reaction led to tetraaqua-bis(5-nitrotetrazolato-N^2)nickel(II) (2.26), which also resulted from the reaction of bis(chloroglyoximato)-nickel(II) with the sodium salt of 5-nitrotetrazole.



Scheme 2.7



2.25



2.26

Ligand exchange has also been observed for other reactions involving bis(glyoximato)nickel(II) complexes by other workers. For example, ^{1}H n.m.r. techniques showed that the reaction of bis(2,3-bornanedione dioximato)nickel(II) ($Ni(LH)_2$) with benzylmethylglyoxime ($L'H_2$) leads to a mixture, the equilibrium composition of which corresponds to $Ni(LH)_2$: $Ni((LH)(L'H)$: $Ni(L'H)_2$ of 1 : 2.7 : 1.9.[30]

The tetrazolato complexes have also been obtained by the direct reaction of the respective tetrazoles with nickel(II)

chloride. Thus, the complex tetrapyridinebis(5-hydroxytetrazolato)nickel(II) was obtained from the reaction of the 5-hydroxytetrazole with nickel(II) chloride in pyridine. Similarly, tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) was prepared from the reaction of the sodium salt of 5-nitrotetrazole with nickel(II) chloride.

The structure of tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) has been studied by X-ray crystallography, and the results obtained are presented in Section 2.7.

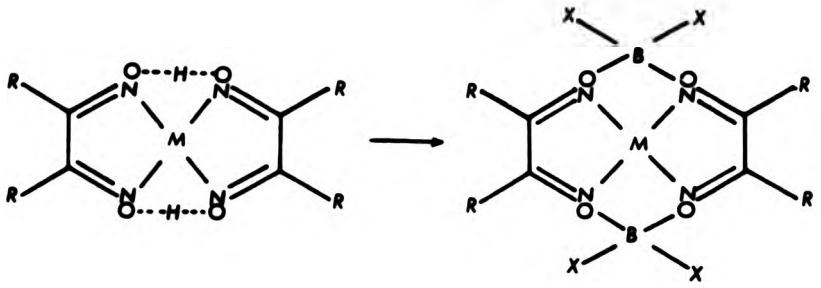
Tetrapyridinebis(5-hydroxytetrazolato)nickel(II) has a magnetic moment of 3.11 μ_B, which is indicative of an octahedral structure.[44] Its electronic spectrum shows absorption maxima at 266, 352, 428, and 558 nm.

2.3.4 Formation of Clathrochelates Involving Diaminoglyoxime

It is well established that various glyoximato complexes react with compounds such as boron trifluoride, tin tetrachloride, or silicon tetrachloride to give clathrochelates of type 2.27 (Reaction 2.1).[8, 45, 46]

Clathrochelates of type 2.27 involving the diaminoglyoximato ligand have also been obtained during the present study. Two synthetic routes were used for the formation of these compounds. In the case of the clathrochelate derived from boron trifluoride, bis(diaminoglyoximato)nickel(II) was treated directly with the fluoro compound in diethyl ether.

In the second approach, diaminoglyoxime, nickel(II) chloride, and boric acid, were allowed to react in water, and ethanol to give clathrochelates of type 2.27 where X= OH, and OC_2H_5. Significantly, in the reaction of boron trifluoride with the nickel(II) complex of diaminoglyoxime, the Lewis acid does not react with the amino groups of the coordinated ligand.



2.27

R= e.g., Me; M= e.g., Ni; X= e.g., F

Reaction 2.1

The characterisation of the clathrochelates formed in this study is based on their elemental analyses, and i.r. spectra. Attempts to obtain mass spectra of these compounds show that these undergo decomposition prior to ionisation.

In the i.r. spectra of these compounds, the bands attributed to C=N (1600 - 1615 cm^{-1}) and N-O (960 - 970 cm^{-1}) are not significantly shifted by the introduction of a different substituent on the boron atom. However, these bands appear at considerably different frequencies compared to those in the $Ni(dagH)_2$ (c.f. Chapter 1, Figure 1.4).

2.4 Spectroscopic Properties of the Dioximes

Infrared absorption bands of the new dioximes are presented in Table 2.5. The OH-stretching bands occur at 3260 - 3540 cm^{-1}. These tend to be broad due to hydrogen bonding. The OH-bending bands appear between 1380 - 1460 cm^{-1}, as observed previously for other dioximes.[47] Each of the investigated dioximes shows a single weak-moderate stretching band around 1650 cm^{-1}, which has been assigned to the C=N bond. Similar compounds, such as methylglyoxime, and dimethylglyoxime show weak bands due to C=N at 1621 cm^{-1}.[15] This C=N stretching band has been attributed to the s-trans form of the anti-dioximes. For amphi-chloroglyoxime, a C=N band attributed to the s-cis form appears as a doublet at 1626 cm^{-1}.[15]

In the ^{1}H n.m.r spectra of the dioximes the chemical shifts of the oximic protons vary between 8.3 and 14.1 ppm. The observed chemical shifts are comparable to those of the oximic proton resonances in other dioximes which range between 4.7 and 14.7 ppm. For example, the chemical shifts for the oximic protons in amphi bis(diisopropylamino)-glyoxime,[1] diaminoglyoxime,[2] and 2-chloro-1,2-dihydroxyimino-ethane-N-pyridinium chloride,[5] are 4.7, 10.0, and 14.7 ppm, respectively. Furthermore, in compounds where the oximic group is substituted, such as the diaminoglyoxime O-diacetate, no signal appears on their ^{1}H n.m.r spectra in this region.[2] The NH protons appear at lower chemical shifts

than the NH_2 protons. These appear to be broader than the oximic protons, which is a typical feature of hydrogens bonded to nitrogen. This is because the large quadropole moment of the nitrogen nucleus induces shortened nuclear spin relaxation times. The amino protons have also been identified by deuterium exchange. In all the new dioximes, the observed integral ratios are in accordance with the suggested structures. In addition, the resonances of the aromatic protons of the substituted groups in these dioximes exhibit characteristic spin-spin splittings. For example, in the ^1H n.m.r spectrum of 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime (2.20), the resonances at 8.4 and 7.8 ppm appear as two doublets, caused by intramolecular hydrogen bonding.

The u.v. spectra of the investigated dioximes in methanol show maximum absorptions at around 230 nm (Table 2.6). These are in accordance with the u.v. spectra of other dioximes in ethanol such as methylglyoxime (λ_{max}= 230 nm), dimethylglyoxime (λ_{max}= 227 nm), and dichloroglyoxime (λ_{max}= 236 nm).[15] The molar extinction coefficients (ϵ_{max}) for these curves are in the range of 963 - 1890 $m^2\ mol^{-1}$, except in the case of 2,3-dioximino-piperazine (2.6; X= H). On the basis of the u.v. results, it can be suggested that these new dioximes, except 2,3-dioximino-piperazine, have the <u>s-trans</u> configuration in solution. Dioximes which cannot assume such a configuration, such as 2,3-dioximino-piperazine, and cyclohexaneglyoxime,[15] show significantly

lower molar absorptivities at the maximum.[15]

Table 2.5 Selected Infrared Absorption Bands of Some Dioximes[1]

Dioxime R	R'	ν(OH) str. (cm^{-1})	ν(OH) bend. (cm^{-1})	ν(C=N) str. (cm^{-1})
H	Cl	3290(m)	1400(m)	1610(s)
Cl	Cl	3260(m)	1410(m)	1615(s)
NH_2	NH_2	3410(m)	1435(s)	1640(s)
$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	3360(m)	1430(m)	1610(s)
$C_6H_3(NO_2)_2NH$	NH_2	3405(m)	1420(m)	1610(s)
$C_6H_2(NO_2)_3NH$	NH_2	3385(s)	1405(m)	1605(m)
$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	3370(s)	1405(m)	1640(s)
$C_6H_5C(H)N$	NH_2	3375(m)	1440(m)	1605(m)
H	tH	3400(m)	1445(m)	1640(m)
H	tCl	3380(m)	1430(m)	1610(s)
tH	tH	3445(m)	1415(s)	1620(m)
tCl	tCl	3540(m)	1380(m)	1630(s)
2.6 (X= H)		3415(m)	1380(m)	1610(m)

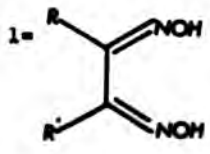


Table 2.6 Ultraviolet Absorption Data of Some Dioximes

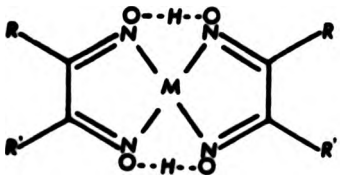
Dioxime		Ultraviolet Absorption Data	
R	R'	λ_{max} (nm)	ϵ_{max} (m^2 mol^{-1})
$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	228	1817
		256	2575
		302	1495
		378	1350
$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	231	1158
		265	877
		396	212
$C_6H_3(NO_2)_2NH$	NH_2	232	1647
		314	748
$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	202	1890
		233	2781
		262	57
$C_6H_5C(H)N$	NH_2	229	963
		267	1025
NH_2	NH_2	234	1551
2.6 (X= H)		201	522
		220	565
		240	630

2.5 Copper(II) and Nickel(II) Complexes of the New Dioximes

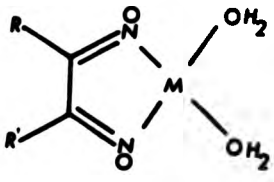
The complexation behaviour of the new dioximes, towards copper(II) and nickel(II) salts has been examined.

Generally, the complexes were prepared by the reaction of the dioxime with the metal(II) acetate in aqueous alcohol, at temperatures ranging from 20 to 60 ^{o}C, and the yield of the product was in the range 40 - 95%. Most of the dioximes reacted readily to give either complexes which contain (i) two dioxime monoanions per metal atom (2.28), or (ii) complexes which contain one dioxime dianion per metal atom (2.29). 1,2-Di(phenyl-N-amino)glyoxime, and 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime reacted with copper(II) acetate to give products of ill-defined composition.

Compounds of type 2.29 were obtained from the tetrazolyl-substituted dioximes. In such complexes, no other anion is present, which implies that the dioxime must be dianionic. Complexes of this type are not very common. On the other hand, complexes of the type 2.28 are very common.



2.28



2.29

2.6 Structures and Properties of the Copper(II) and Nickel(II) Glyoximato Complexes

Some properties of the copper(II) and nickel(II) glyoximato conplexes formed in the present study are summarised in Tables 2.7 and 2.8.

The copper(II) complexes were generally green or brown, whereas colours of the nickel(II) complexes varied from light green to burgundy.

All the copper(II) and nickel(II) complexes have very low solubility in water and in common organic solvents such as acetone, methanol, and dimethylformamide. The complexes derived from the tetrazolyl-substituted dioximes, when treted with dilute sulphuric acid, readily gave the respective free ligands.

Thermal studies on the complexes of the modified dioximes show that some of these compounds decompose slowly without melting at high temperatures (>300 ^{o}C). However, the copper(II) complexes generally decompose at lower temperatures. The thermal behaviour of the copper(II) and the nickel(II) complexes and their thermal kinetic parameters have been studied in detail, and the results are discussed in Chapter 4.

The i.r. spectra of the complexes of the complexes prepared during the present study exhibit C=N absorption bands at

values lower than those found in the i.r. spectra of their corresponding ligands. For example, in the i.r. spectrum of free 1-(5-chlorotetrazolato)glyoxime the C=N absorption band is at 1610 cm^{-1}, whereas in the i.r. spectrum of the corresponding copper(II) complex of this ligand, this band appears at 1590 cm^{-1}. However, in the i.r. spectra of many of the complexes investigated, more than one band appears in the 1600 cm^{-1} region, and assignment of the ν(C=N) is thus not possible. The presence of coordinated water molecules in the complexes of the tetrazolyl-substituted dioximes is suggested by the presence of broad absorption bands in the region of 3400 - 3600 cm^{-1}.

Table 2.7 Some Properties of the Metal(II) Complexes ($M(LH)_2$) of Some Dioximes (LH_2)

Compound Number	Dioxime, LH_2 R	R'	Metal	Colour	Magnetic Moment (μ_B)	M.p., (^oC) (dec.)
1	C_6H_5NH	C_6H_5NH	Ni	Brown	diam.[1]	261
2	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Ni	Orange	diam.[1]	293
3	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Cu	Brown	2.12	269
4	$C_6H_3(NO_2)_2NH$	NH_2	Ni	Orange-Brown	3.33	261
5	$C_6H_3(NO_2)_2NH$	NH_2	Cu	Green	1.59	217

Table 2.7 (continued)

Compound Number	R	R'	Metal	Colour	Magnetic Moment (μ_B)	M.p., (^oC) (dec.)
6	$C_6H_2(NO_2)_3NH$	NH_2	Ni	Green	3.40	225
7	$C_6H_5C(H)N$	NH_2	Ni	Burgundy	2.85	201
8	$C_6H_5C(H)N$	NH_2	Cu	Brown	1.36	213
9	2.6 (X= H)		Ni	Brown	diam.[1]	___
10	2.6 (X= H)		Cu	Brown-Green	1.46	___

[1]diamagnetic

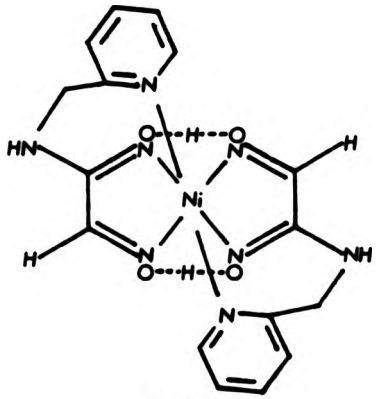
Table 2.8 Some Properties of the Metal(II) Complexes ($M(L).2H_2O$) of Some Dioximes (LH_2)

Compound Number	Dioxime, LH_2 R	R'	Metal	Colour	M.p., (^oC) (dec.)
11	tH	tH	Ni	Green	174
12	tH	tH	Cu	Green	122
13	tCl	tCl	Ni	Brown-Green	150
14	tCl	tCl	Cu	Green	131
15	tH	H	Cu	Brown-Green	97
16	tCl	H	Cu	Brown	147

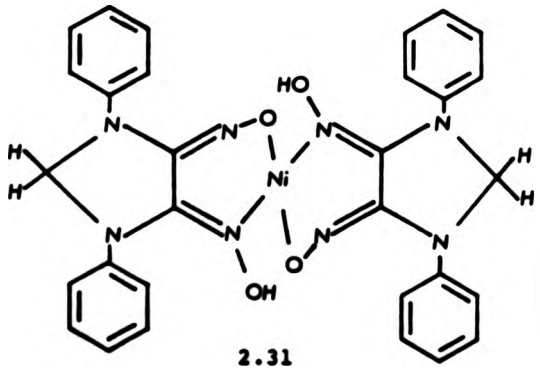
Among the nickel(II) complexes of type 2.28, the complexes of 1,2-di(phenyl-N-amino)glyoxime (1), 1,2-di(3-nitrophenyl-N-amino)glyoxime (2), and 2,3-dioximino-piperazine (9) are diamagnetic. Diamagnetism is a typical feature of planar nickel(II) complexes of dioximes,[48, 49] the structure of which have been confirmed in several cases by X-ray studies.[50, 51] Thus, it may be suggested that the nickel(II) complexes found to be diamagnetic in this study are also planar. On the other hand, the nickel(II) complexes of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (4), 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime (6), and 1-amino-2-(benzyl-N-amino)glyoxime (7) are paramagnetic and this implies that these complexes do not have a square planar structure. In the past, only a few nickel(II) glyoximato complexes have been found to be paramagnetic. For example, the magnetic moment of the nickel(II) complex of N-(2-methylpyridyl)aminoglyoxime (2.30) is 1.26 μ_B,[52] and that of 1,3-diphenyl-4,5-bis(hydroxyimino)imidazolidine (2.31) is 3.14 μ_B.[53] In the former case, deviation from planarity is suggested to occur because of weak bonds between the donor pyridyl groups and the nickel atom, which leads to an octahedral arrangement. In the case of the nickel(II) complex of 1,3-diphenyl-4,5-bis(hydroxyimino)imidazoline, deviation from planarity has been correlated to the non-planar configuration of the ligand itself. In addition, the nickel(II) complexes of 1,2-di(2,4,6-trinitrophenyl-N-amino)-glyoxime, and 1-amino-2-(2,4,6-trinitrophenyl-N-amino)-glyoxime (6) were previously found to be paramagnetic

(magnetic moment= 3.29, and 3.44 μ_B, respectively).[5]

In the case of the nickel(II) complexes of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (4), and 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime (6), deviation from planarity may be due to intramolecular bonding between nitro groups and the nickel atom. However, intermolecular association involving nitro groups and nickel atoms of neighbouring complex molecules cannot be precluded. In the case of bis((1-amino-2-benzyl-N-imino)glyoximato)nickel(II) (7), the complex may have a tetrahedral structure, or association may be present.

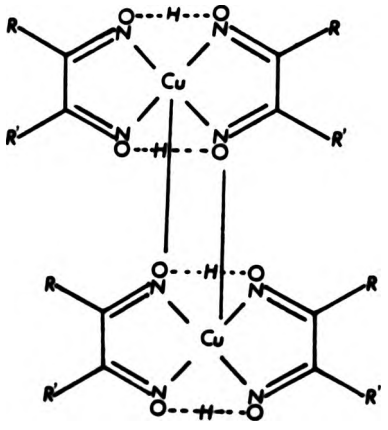


2.30



2.31

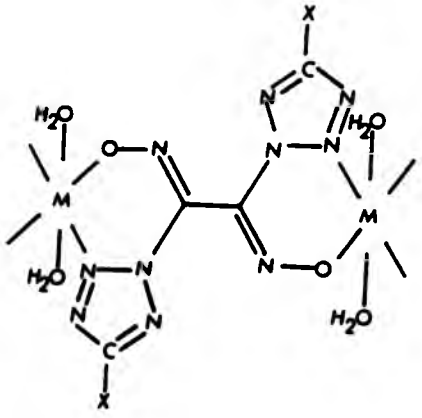
The magnetic moment of the copper(II) complex of 1,2-di-(3-nitrophenyl-N-amino)glyoxime (3) is within the expected region for a magnetically dilute copper(II) species (1.75 - 2.20 μ_B),[37] but those of the copper(II) complexes of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (5), 1-amino-2-(benzyl-N-imino)glyoxime (8), and 2,3-dioximino-piperazine (10) are lower. The low magnetic moments of the latter sugggest that there may be some association between the respective complex molecules as found for other copper(II) dioximates (2.32).[54] Previously, the magnetic moment of bis(1,2-di(2,4,6-trinitrophenyl-N-amino)glyoximato)copper(II) was also found to be low (1.63 μ_B).[5]



2.32

The tetrazolyl-substituted dioximes led to copper(II) and nickel(II) complexes of the type 2.29, containing the dianion

of the dioxime. The nickel(II) complex of amphi benzilglyoxime is the only example of a complex containing the dianion of a dioxime.[12] The complexes of tetrazolyl-substituted dioximes were formulated on the basis of their elemental analyses and i.r. spectra. Further analyses of these compounds were limited due to their explosive nature. Their structures can be tentatively represented as shown in 2.33. In such complexes, the oximic groups as well as the tetrazolyl substituents of the ambidentate ligands participate in metal chelation. Analogous structures have been proposed for metal(II) complexes of the dithiooxamides.[55]

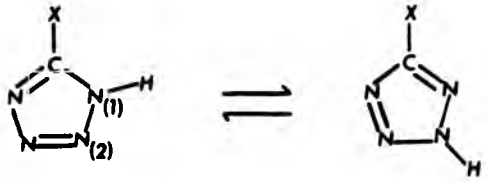


2.33

2.7 The X-ray Crystallographic Study of Tetraaquabis(5-nitrotetrazolato-N^2)nickel(II)

During the last few years, there has been an enormous development in the chemistry of tetrazoles and their complexes.[56-59] Present interest in these compounds is mainly due to their thermal characteristics. Many complexes of 5-substituted tetrazoles exhibit explosive properties, and some tetrazole compounds such as lead azotetrazole, tetracene, and copper nitrotetrazole have been used as explosive primers.[60, 61]

Tetrazoles may exist in two tautomeric forms (2.34 - 2.35), and their anions are thus ambidentate.[56, 62]



2.34 2.35

X-ray crystal structures have been reported for only a few tetrazolato complexes, and these show that the anion of a tetrazole may bond to a metal either through N1 or N2. For example, the structure of bis[dimethyl(phenyl)phosphine]bis-(5-methyltetrazolato)palladium(II) shows that both tetrazole rings are N(1) bonded,[63] whereas that of pentammine(5-

cyanotetrazolato-N^2)cobalt(III) perchlorate shows that the tetrazole ring is N(2) bonded to the metal.[64]

During the present study, the structure of tetraaquabis(5-nitrotetrazolato-N^2)nickel(II), obtained by ligand exchange reactions between both the nickel(II) complexes of amphi-chloroglyoxime and diaminoglyoxime with the sodium salt of 5-nitrotetrazole dihydrate, has been studied by X-ray crystallography.

The structure of a molecular unit of tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) is presented in Figure 2.1.

In the complex, each nickel atom is in a trans octahedral environment with two 5-nitrotetrazolato rings and four water molecules. The 5-nitrotetrazolato rings bond to the nickel through the N(2) nitrogens, and are planar. These are related by the twofold axis. A site of 2/m symmetry for the nickel atom was derived using the Patterson map. The final atomic fractional coordinates are given in Table 2.9. Bond lengths and angles are listed in Tables 2.10, and 2.11, respectively. Additional data for the structure of tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) are found in the Appendix. Within the tetrazole ring, the C-N (1.305, and 1.320 Å) and (N-N 1.338, 1.308, and 1.345 Å) bond distances are all shorter than those found for the respective single bonds (C-N= 1.48 Å; N-N= 1.45 Å).[65] This suggests that there is considerable electron delocalisation in these tetrazole rings, which is analogous to the structures of other

tetrazoles and tetrazolato complexes.[66-68] The N(3)-N(2) bond length (1.308 Å) is shorter than the other two N-N bond lengths which implies greater electron density localisation in the former. Hydrogen bonding is evident from the short intermolecular distance between H(1w) and N(4) (-1/2-x, y, -1/2-z) (2.19 Å). Thus, linking of adjacent complex molecules occurs. The bond angles within the tetrazolato ring [N(3) - N(2) - N(1)= 111.0°; C(1) - N(4) - N(3)= 102.4°; N(4) - N(3) - N(2)= 108.9°; N(4) - C(1) - N(1)= 115.8°; C(1) - N(1) - N(2)= 101.9°] are similar to that of a regular pentagon (108°). The nitro-substituent of the tetrazolato ring does not participate in any bonding with the nickel. This is in contrast to the structure of mercuric 5-nitrotetrazolate, in which the nitro-substituent coordinates to the mercury atom.[69]

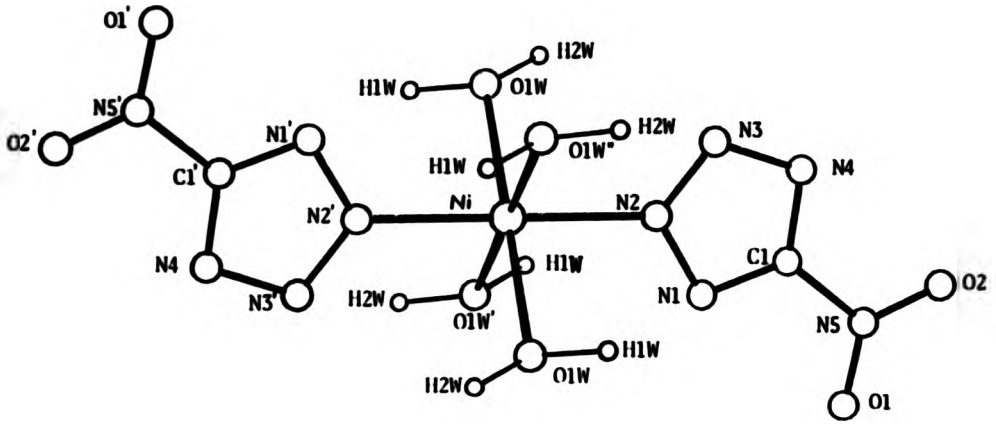


Figure 2.1 Atomic Arrangement in Tetraquabis(5-nitrotetrazolato-N^2)nickel(II) ($Ni(tNO_2)_2(H_2O)_4$)

Table 2.9 Fractional Atomic Coordinates and Thermal Parameters ($Å^2$) for $Ni(tNO_2)_2(H_2O)_4$

Atom	x	y	z	U_{iso} or U_{eq}
Ni	0	0	0	0.0337(7)
N(1)	0	0.1403(4)	-0.1653(6)	0.044(4)
N(2)	0	0.0595(4)	-0.1564(5)	0.038(4)
N(3)	0	0.0254(3)	-0.2556(6)	0.044(4)
N(4)	0	0.0834(4)	-0.3348(5)	0.044(4)
C(1)	0	0.1503(4)	-0.2741(6)	0.037(4)
N(5)	0	0.2301(5)	-0.3258(8)	0.067(6)
O(1)	0	0.2879(4)	-0.2640(9)	0.122(8)
O(2)	0	0.2335(4)	-0.4269(6)	0.094(6)
O(1w)	-0.2188(8)	0.0804(2)	0.0587(4)	0.069(3)
H(1w)	-0.313	0.093	-0.017	0.08
H(2w)	-0.304	0.068	0.136	0.08

Table 2.10 Bond Lengths (Å) for $Ni(tNO_2)_2(H_2O)_4$

Ni	-N(2)	2.105(6)	Ni	-O(1w)	2.125(5)
N(1)	-N(2)	1.338(9)	N(1)	-C(1)	1.305(10)
N(2)	-N(3)	1.308(9)	N(3)	-N(4)	1.345(9)
N(4)	-C(1)	1.320(10)	C(1)	-N(5)	1.454(11)
N(5)	-O(2)	1.204(12)	N(5)	-O(1)	1.205(12)

Table 2.11 Bond Angles (°) for $Ni(tNO_2)_2(H_2O)_4$

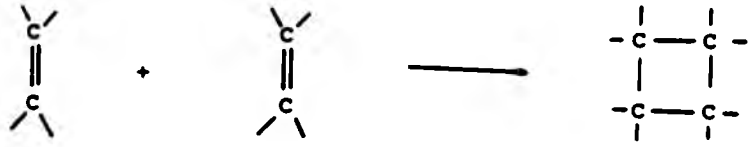
O(1w)	-Ni	-N(2)	89.9(2)
O(1w)	-Ni	-O(1w'')	89.9(3)
O(1w)	-Ni	-N(2')	90.1(2)
N(1)	-N(2)	-Ni	122.4(5)
N(3)	-N(2)	-N(1)	111.0(6)
C(1)	-N(4)	-N(3)	102.4(6)
N(5)	-C(1)	-N(1)	122.3(7)
O(2)	-N(5)	-C(1)	117.7(8)
O(1)	-N(5)	-O(2)	124.9(8)
N(2)	-Ni	-N(2')	180.0(2)
O(1w)	-Ni	-O(1w''')	90.1(3)
O(1w)	-Ni	-O(1w')	180.0(2)
N(3)	-N(2)	-Ni	126.6(5)
N(4)	-N(3)	-N(2)	108.9(6)
N(4)	-C(1)	-N(1)	115.8(7)
N(5)	-C(1)	-N(4)	121.9(7)
C(1)	-N(1)	-N(2)	101.9(6)
C(1)	-N(5)	-O(1)	117.4(8)

2.8 Reactions of Copper(II) and Nickel(II) Glyoximato Complexes with Dimethyl Acetylenedicarboxylate

2.8.1 Introduction

Cycloaddition reactions have been applied for the synthesis of a wide variety of heterocyclic compounds.[70-73] Such reactions may lead to four-, five-, and six-membered heterocyclic compounds.

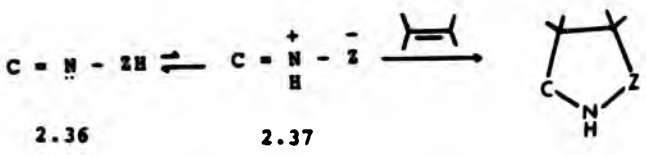
Four-membered cyclic compounds may be formed by [2 + 2] reactions, which are effected both thermally and photochemically (Reaction 2.2).[70]



Reaction 2.2

The synthesis of five-membered heterocyclic compounds can be achieved by [2 + 3] processes, involving cycloadditions of 1,3-dipoles (2.36, 2.37) (Reaction 2.3).[74, 75] In reactions of this type, a 1,3-dipole is generated by an intramolecular proton transfer, otherwise called prototropy. Proton transfer

processes can occur under thermal or photochemical influence, or in the presence of an acid, base, transition metal, or transition metal complex.[75]

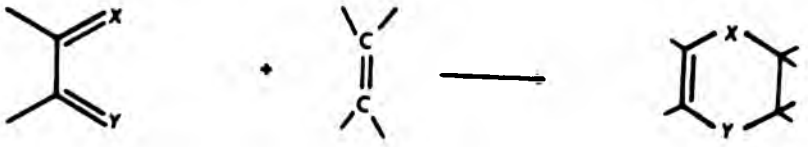


2.36 2.37

where, Z= e.g., O, NR

Reaction 2.3

The common Diels-Alder reaction, often referred to as a [4 + 2] cycloaddition reaction, involves the reaction of a diene or a heterodiene with a dienophile to give six-membered cyclic products (Reaction 2.4).[76]



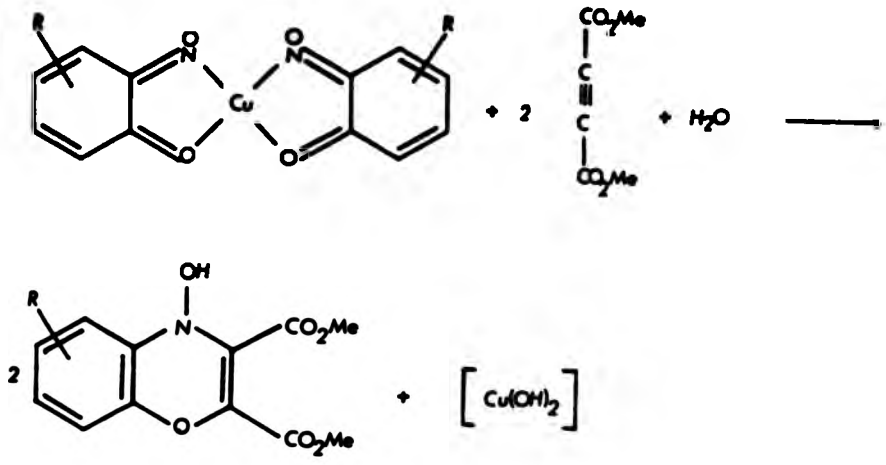
where, X, Y= e.g., CH_2, N

Reaction 2.4

Electron-deficient acetylenes, such as dimethyl acetylenedicarboxylate (DMAD), have often been used in Diels-Alder and 1,3-dipolar reactions. Such reactions will be discussed in more detail in the subsequent sections.

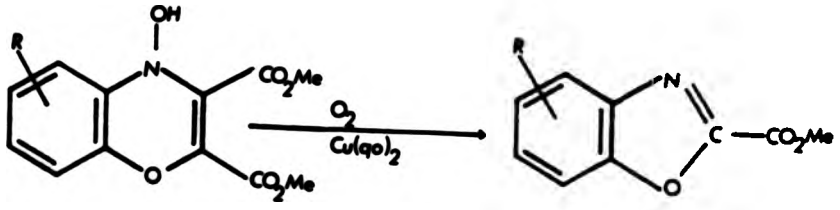
Reactions of 1,2-Quinone Mono-oximes and Their Metal Complexes with Dimethyl Acetylenedicarboxylate

Copper(II) complexes of 1,2-quinone mono-oximes react readily with dimethyl acetylenedicarboxylate in 1,2-dimethoxyethane and in the presence of water, to give 1,4-benzoxazines in high yields.[77] The reaction involves cycloaddition across the heterodiene function rather than across the diene function of the complex. Water participates in these reactions as represented in Scheme 2.8. The hydroxide which is formed may then cause hydrolysis of the ester functions of the 1,4-benzoxazine or of dimethyl acetylenedicarboxylate to give various by-products.



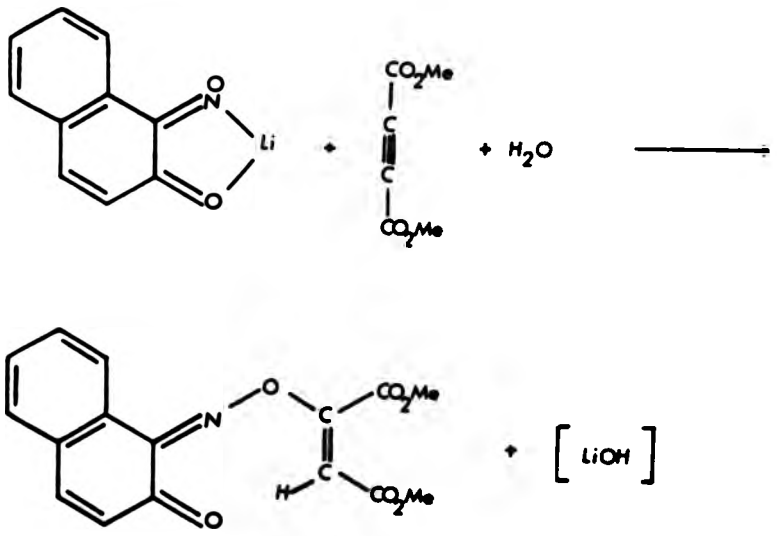
Scheme 2.8

Other studies of 1,2-quinone mono-oximato copper(II) complexes with dimethyl acetylenedicarboxylate have indicated that when the reaction is carried out in anhydrous methanol a benzoxazole is formed.[78] However, subsequent studies have established that this is a secondary product arising by the $Cu(qo)_2$-catalysed aerobic oxidation of the 1,4-benzoxazine (Scheme 2.9).[79]



Scheme 2.9

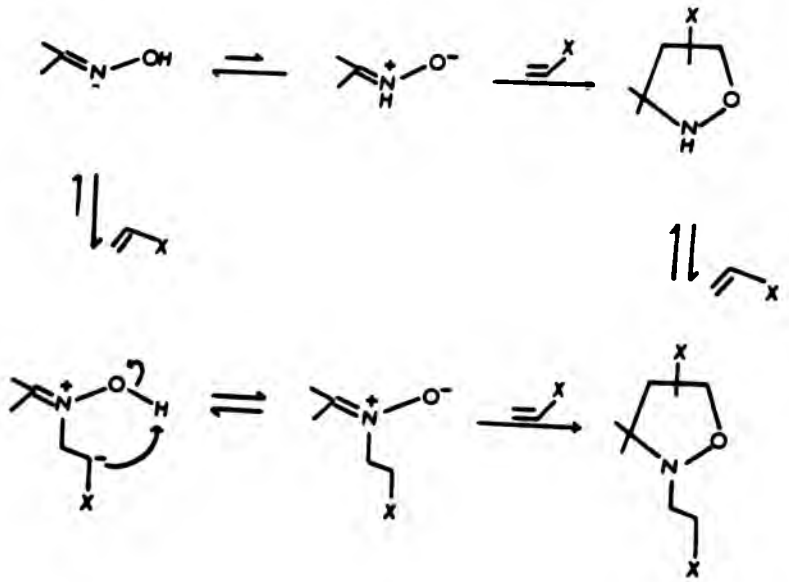
Dimethyl acetylenedicarboxylate does not react with the 1,2-quinone mono-oximes, their methyl esters or their cobalt(III) complexes,[77] and reacts only slowly with their nickel(II) complexes to give 1,4-benzoxazines.[78] In contrast, dimethyl acetylenedicarboxylate reacts readily with lithium 1,2-quinone mono-oximates to give nucleophilic addition products, otherwise referred to as a Michael addition products (Scheme 2.10).[79] In the case of the lithium complex derived from 1,2-naphthoquinone 2-oxime, the cycloadduct is also formed. Again water participates in these reactions and the metal hydroxide formed may cause hydrolysis of the ester groups in the corresponding adduct or dimethyl acetylene-dicarboxylate.



Scheme 2.10

1,3-Dipolar Cycloaddition Reactions of Oximes

Aldehyde and ketone oximes undergo 1,3-dipolar cycloaddition reactions with olefins and acetylenes to give the 2:1 adducts, isoxazolidines.[75, 80-83] Consecutive Michael addition and cycloaddition occur either intermolecularly or intramolecularly, thus leading to different types of 2:1 adducts. The fact that Michael addition to the oxime nitrogen occurs first explains the formation of the 2:1 adduct rather than any 1:1 adduct (Scheme 2.11). The structure of a 2:1 isoxazolidine adduct, obtained from the reaction of benzaldehyde oxime and acrylonitrile was previously confirmed by an X-ray crystallographic study.[80]



Scheme 2.11

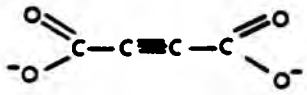
In contrast to the simple aldehyde and ketone oximes, the 2-oximes of 1,2,3-tricarbonyl systems undergo cycloadditions with the dipolarophile N-phenylmaleimide.[84] In oximes of this type, steric interactions involving the carbonyl groups prevent Michael addition.

In spite of the extensive work reported on cycloaddition reactions of oximes, and 1,2-quinone mono-oximes and their complexes, there has so far been no report of analogous reactions with dioximes or their complexes. The present work deals with the reaction of dimethyl acetylenedicarboxylate with diaminoglyoxime, diphenylglyoxime, dimethylglyoxime, cyclohexaneglyoxime, and their copper(II) and nickel(II) complexes. These studies were prompted by the processes observed in the reactions of oximes, and 1,2-quinone mono-oximes with acetylenes such as dimethyl acetylenedicarboxylate.

2.8.2 Reaction of Dioximes and Their Copper(II) and Nickel(II) Complexes with Dimethyl acetylenedicarboxylate

The reaction of bis(diaminoglyoximato)nickel(II) with dimethyl acetylenedicarboxylate in aqueous 1,2-dimethoxyethane (DME) was investigated in different molar ratios and at different temperatures. The system involving the reactants in 1:2 molar ratio at 20 ^{o}C was slow, and an i.r. examination of the resulting metal-containing residue indicated the presence of unreacted bis(diaminoglyoximato)-nickel(II). In the 1:4 ratio reaction at 20 ^{o}C, the yield of the organic product was higher. The reaction afforded a brown nickel-containing residue and a cream organic product. The nickel-containing solid is insoluble in common organic solvents such as methanol and acetone. The i.r. spectrum of this solid is simple and includes absorption bands at 3400 and 1640 cm^{-1} indicative of the presence of OH and C=O groups, respectively. This is very similar to the i.r. of the metal-containing products obtained in analogous reactions of metal(II) complexes of 1,2-quinone mono-oximes. In addition, this resembles the i.r. spectra of the metal-containing products obtained from the reactions of the other glyoximato complexes with dimethyl acetylenedicarboxylate investigated in the present study. Also, this is similar to the i.r. spectrum of the hydrated copper(II) derivative of the carboxylate dianion 2.38, which was obtained by the direct

reaction of copper(II) hydroxide with dimethyl acetylene-dicarboxylate (Figure 2.2). On the basis of these results, it can be suggested that the metal-containing product in these reactions is a mixture of the metal(II) hydroxide and the metal(II) derivative of the dianion of hydrolysed dimethyl acetylenedicarboxylate (2.38).



2.38

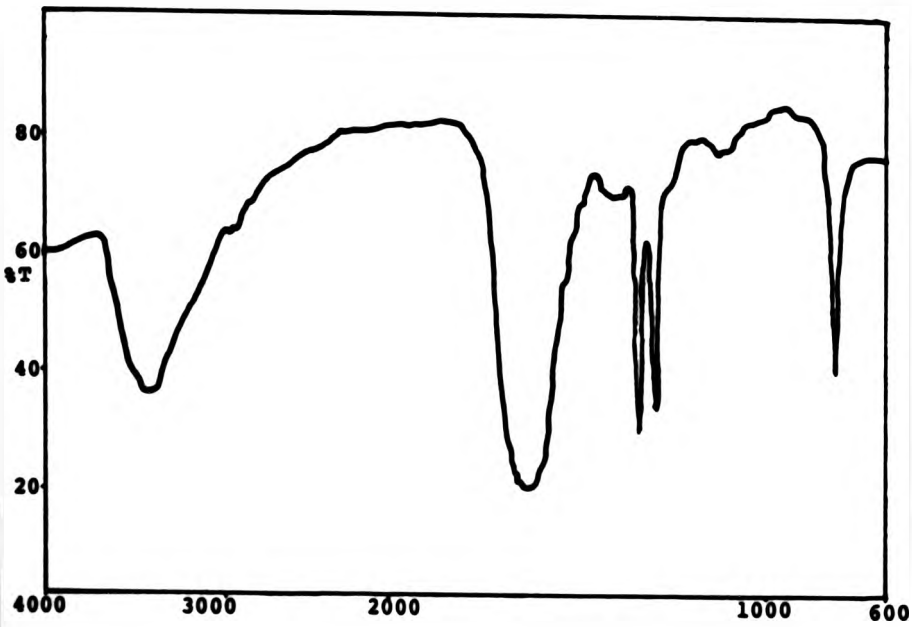
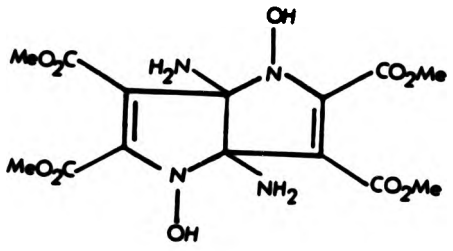
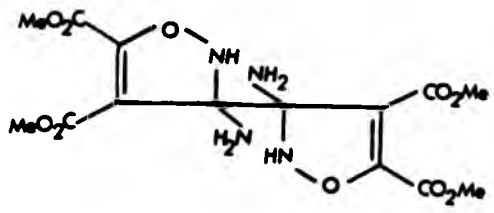


Figure 2.2 I.r. Spectrum of the Copper(II) Derivative of the Carboxylate Dianion 2.38

The reaction of bis(diaminoglyoximato)nickel(II) with dimethyl acetylenedicarboxylate also led to the formation of a white solid. This was characterised on the basis of its elemental analysis, ^1H n.m.r., i.r., and m.s. spectra. Its elemental analysis suggests the presence of two DMAD moieties per one $dagH_2$ unit. There exist two possible structural formulae for this compound (2.39, and 2.40).



2.39



2.40

The structure shown in 2.40 is precluded on the basis of the EI and isobutane PICI mass spectra of this compound. In the EI mass spectrum of the product, the highest peak, which is of strong intensity, is at m/z 402, suggesting that this is due to the parent ion. This confirms the presence of two DMAD

moieties per one $dagH_2$ unit. Peaks arising from loss of $MeO^{\cdot}$, $MeCO_2^{\cdot}$, are present (Table 2.12). The base peak in the EI mass spectrum of this product is at m/z 101, and corresponds to the ion $[dagH_2 - OH]^+$. Significantly, a peak of moderate intensity at m/z 368 is attributed to loss of $2OH^{\cdot}$. Accurate mass measurements confirm that this peak is due to the fragment of elemental composition $[C_{14}H_{16}N_4O_8]^{+\cdot}$, which arises by the loss of $2OH^{\cdot}$. The mass spectrometric results obtained further preclude the structural formulation shown in 2.40, because the EI spectrum of this product does not show a peak at m/z 201, which would be expected to arise by cleavage of the bicyclic compound of type 2.40. The isobutane PICI spectrum of this product shows a peak of low intensity at m/z 403 due to the ion $[M + H]^+$ (Figure 2.3). Fragments analogous to those obtained under EI conditions are present in this spectrum.

Table 2.12 Ion Abundances in the EI Mass Spectrum of the 2:1 Adduct 2.39

m/z	Intensity (%)	Assignment
402	14	$[M]^{+\cdot}$
371	3	$[M - MeO]^+$
368	20	$[M - 2OH]^{+\cdot}$
343	2	$[M - MeCO_2]^+$
284	12	$[M - MeCO_2]^+$
101	100	$[dagH_2 - OH]^+$
59	66	$[MeCO_2]^+$

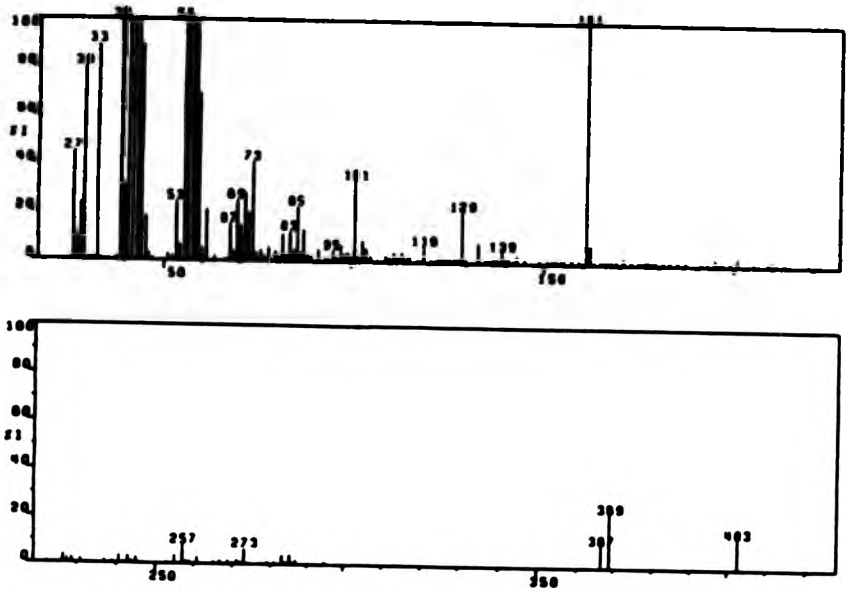


Figure 2.3 Isobutane PICI Mass Spectrum of the 2:1 Adduct 2.39

The ^1H n.m.r. spectrum of the product supports its formulation. This shows a singlet at 6.0 ppm, a doublet at 3.7 - 3.8 ppm, and a singlet at 2.8 ppm in the ratio of 2:6:1 (Figure 2.4). The signals at 6.0 and 2.8 ppm exchange with D_2O, thus indicating that these are due to the NH_2, and OH protons, respectively. Consequently, on the basis of their integral ratio, the signals at 3.7 - 3.8 ppm are assignable

to the Me protons. The latter assignment is supported by the ^1H n.m.r. spectra of other cycloaddition products obtained by reactions of oximes with dimethyl acetylenedicarboxylate, in which the Me protons have been found to give signals in the region of 3.8 - 4.1 ppm.[85] The i.r. spectrum of the compound offers further support for the proposed formulation (Figure 2.5). This includes two sharp bands at 3475 and 3365 cm^{-1}, due to ν(OH), and $\nu(NH_2)$. A band at 1710 cm^{-1} is due to ν(C=O).

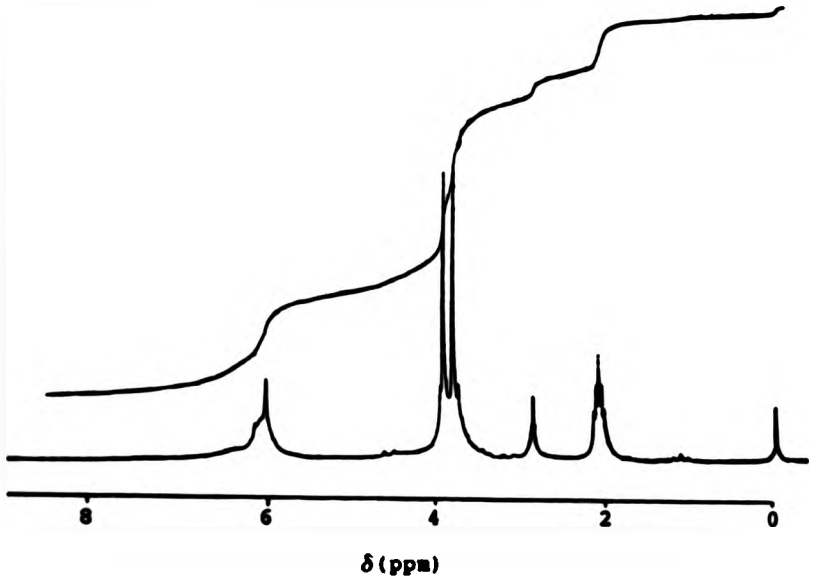


Figure 2.4 ^1H n.m.r. Spectrum of the 2:1 Adduct 2.39

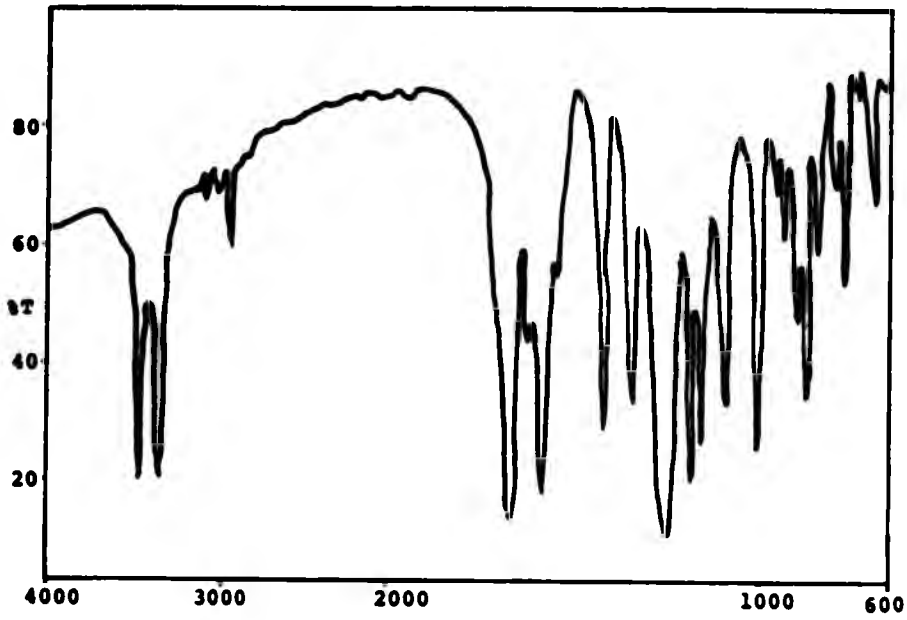


Figure 2.5 I.r. Spectrum of the 2:1 Adduct 2.39

The 2:1 and 1:1 nickel(II) chloride adducts of diaminoglyoxime failed to react with dimethyl acetylenedicarboxylate under the conditions employed. This can be explained in terms of polar effects; the adducts $NiCl_2.dagH_2$ and $NiCl_2.2dagH_2$ are less effective in polarising the diene than $Ni(dagH)_2$, because of the presence of the chloro groups.

The monohydrate copper(II) complex of diaminoglyoxime $Cu(dagH)_2.H_2O$ also reacted with dimethyl

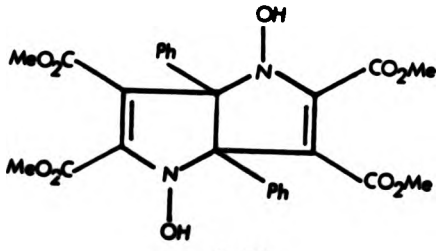
acetylenedicarboxylate, but only in a 1:4 molar ratio and under refluxing conditions. This reaction led to a copper-containing residue, the analysis of which suggests that it is a mixture of copper(II) hydroxide and the copper(II) derivative of the carboxylate dianion 2.38. The cycloaddition product 2.39 was the major product of this reaction, but a t.l.c. examination of the reaction mixture indicated the presence of at least two other products. The yield of 2.39 from the $Cu(dagH)_2.H_2O$/DMAD reaction was significantly lower than that obtained in the $Ni(dagH)_2$/DMAD system.

The reaction of free diaminoglyoxime with dimethyl acetyledicarboxylate in 1:2 molar ratio and in aqueous 1,2-dimethoxyethane, was examined both at 20 ^{o}C and under refluxing conditions. No reaction occured at 20 ^{o}C, probably because of the insolubility of the dioxime. However, diaminoglyoxime reacted readily with dimethyl acetylene-dicarboxylate under refluxing conditions to give a mixture of products which could not be separated. Comparative t.l.c. indicates that this mixture consists of the adduct 2.39 and two other products, neither of which correspond to those obtained from the $Cu(dagH)_2.H_2O$/DMAD system.

The behaviour of the copper(II) and nickel(II) complexes of diphenylglyoxime ($Ni(dPhgH)_2$, and $Cu(dPhgH)_2$), towards dimethyl acetylenedicarboxylate was found to be analogous to that found in the reaction systems involving the nickel(II) and copper(II) complexes of diaminoglyoxime. These failed to react with dimethyl acetylenedicarboxylate in 1:2 molar ratio

at 20 °C, but reacted readily in 1:4 molar ratio under refluxing conditions. In each case, an insoluble metal-containing product resulted. The analytical and spectroscopic results of these residues were similar to those found for the metal-containing residues obtained in the analogous reactions of the diaminoglyoximato complexes. In the case of the reaction involving bis(1,2-diphenylglyoximato)copper(II) and dimethyl acetylenedicarboxylate, the i.r. of the copper-containing solid, is identical to the i.r. of the copper(II) derivative of the carboxylate anion 2.38 (Figure 2.2). Its elemental analysis indicates a copper:carbon ratio of 1:4, and suggests that this is the copper(II) derivative of the carboxylate dianion 2.38.

The major organic product obtained in the reactions of the nickel(II) and copper(II) complexes of diphenylglyoxime with dimethyl acetylenedicarboxylate was formulated to be the 2:1 adduct 2.41 on the basis of its elemental analysis, i.r., ^1H n.m.r., and mass spectra. Like the reactions involving the diaminoglyoximato complexes, product 2.41 resulted from both reactions, but in the case of the reaction involving the copper(II) complex, its yield was much lower.



2.41

The i.r. of the 2:1 adduct 2.41 is fairly complex, and shows absorption bands at 3400 and 1730 cm^{-1} due to ν(OH) and ν(C=O), respectively (Figure 2.6).

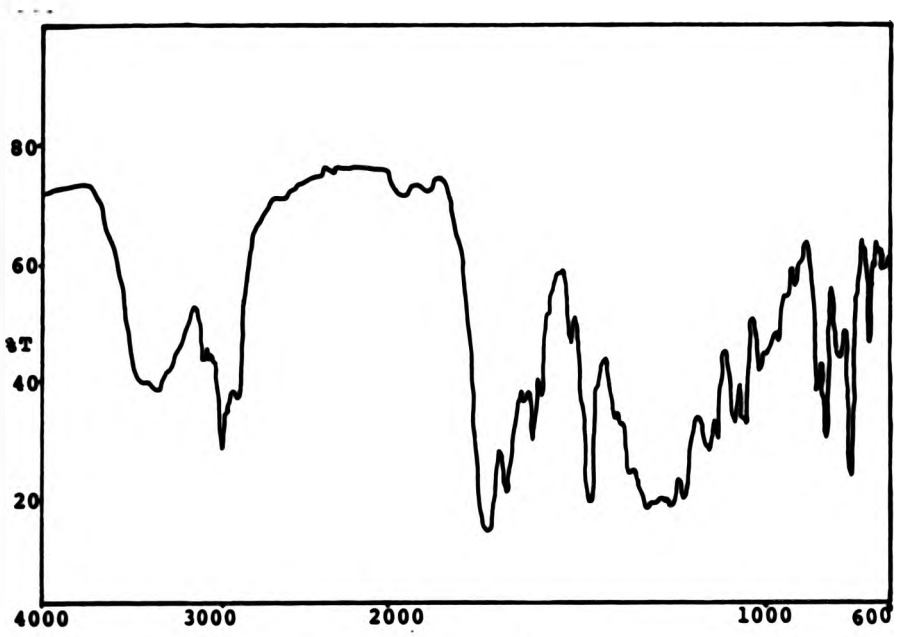


Figure 2.6 I.r. Spectrum of the 2:1 Adduct 2.41

The ^{1}H n.m.r. spectrum of the product shows the expected signals at 7.5 ppm due to the phenyl protons, 3.8 - 4.0 ppm due to the Me protons, and a signal at 2.9 ppm due to the OH protons (Figure 2.7). The assignment of the signal at 2.9 ppm is confirmed by its exchange with D_2O.

The EI mass spectrum of this product shows a peak

corresponding to the parent ion at m/z 524. The fragmentation pattern of this product is similar to that of the cycloadduct 2.39, and includes peaks corresponding to ions arising by loss of $MeO^{\cdot}$, and $MeCO_2^{\cdot}$, (Table 2.13). Furthermore, its isobutane PICI mass spectrum shows a peak of strong intensity due to the ion $[M + H]^+$ (Figure 2.8).

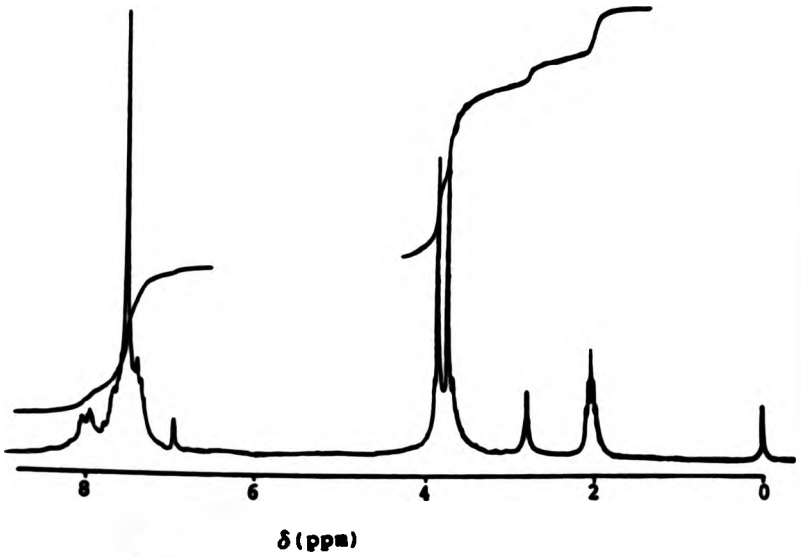


Figure 2.7 ^1H n.m.r. Spectrum of the 2:1 Adduct 2.41

Table 2.13 Ion Abundances in the EI Mass Spectrum of the 2:1 Adduct 2.41

m/z	Intensity (%)	Assignment
524	24	$[M]^{+\cdot}$
465	12	$[M - MeCO_2]^+$
406	11	$[M - 2MeCO_2]^{+\cdot}$
383	28	$[M - 4MeO - OH]^+$
313	66	$[M - 3MeCO_2 - 2OH]^+$
238	41	$[(PhCNO)_2]^{+\cdot}$
105	100	$[PhCNH_2]^{+\cdot}$
59	72	$[MeCO_2]^+$

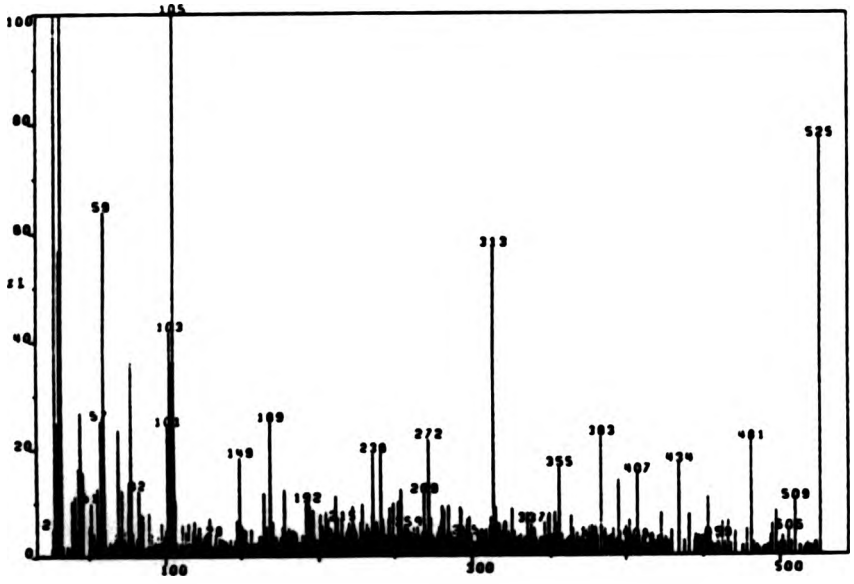


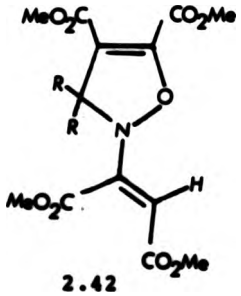
Figure 2.8 Isobutane PICI Mass Spectrum of the the 2:1 Adduct 2.41

Unlike diaminoglyoxime, diphenylglyoxime and dimethylglyoxime failed to react with dimethyl acetylenedicarboxylate in 1,2-dimethoxyethane under similar conditions. All these dioximes exist in the anti form, and thus their differences in behaviour towards dimethyl acetylenedicarboxylate cannot be due to their configuration. Furthermore, it has been previously shown that the stereochemistry of oximes is not important in such reactions, because isomer interconversion is faster than cyclo-addition.[75] The difference in behaviour of these dioximes towards dimethyl acetylenedicarboxylate may be related to intramolecular factors. In the case of diaminoglyoxime, intramolecular hydrogen bonding involving the amino and oxime groups will favour intramolecular 1,2-proton shift.

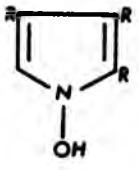
The behaviour of dimethyl acetylenedicarboxylate towards cyclohexaneglyoxime ($chgH_2$) and its nickel(II) complex ($Ni(chgH)_2$) was also also investigated under the conditions used for the analogous reactions involving the acyclic dioximes and their complexes. These reactions were expected to give products of a different type to those obtained using the acyclic dioximes and their complexes, because cyclohexaneglyoxime cannot acquire the s-trans configuration in solution. However, the nickel(II) complex of cyclohexaneglyoxime failed to react with dimethyl acetylenedicarboxylate, probably due to its insolubility. The free dioxime also failed to react, even under forcing conditions.

2.8.3 Mechanistic Appraisal of the Reactions of Copper(II) and Nickel(II) Complexes of Dioximes with Dimethyl Acetylenedicarboxylate

The 2:1 adducts obtained in the cycloaddition of dioximes with dimethyl acetylenedicarboxylate (2.39, 2.41), are different to those obtained from analogous reactions of mono-oximes. In the case of mono-oximes, the 2:1 adducts formed incorporate a second molecule of the dipolarophile on the isoxazolidine N-atom, arising by Michael addition. For example, in the 2:1 adduct formed from cyclohexanone and acetone oximes with dimethyl acetylenedicarboxylate, the second molecule of the dipolarophile is attached to the isoxazolidine N-atom (2.42).[85] As discussed in Section 2.8.1, the process of mono-oxime cycloaddition consists of consecutive Michael addition and cycloaddition. In the case of dioximes, cycloaddition occurs on both oximic groups. Fused N-hydroxypyrroles analogous to those obtained in the present study have not been previously reported. However, N-hydroxypyrroles of the type 2.43 are widely known, and may be prepared from the oximes of α-haloketones and β-keto-esters.[86]



2.42

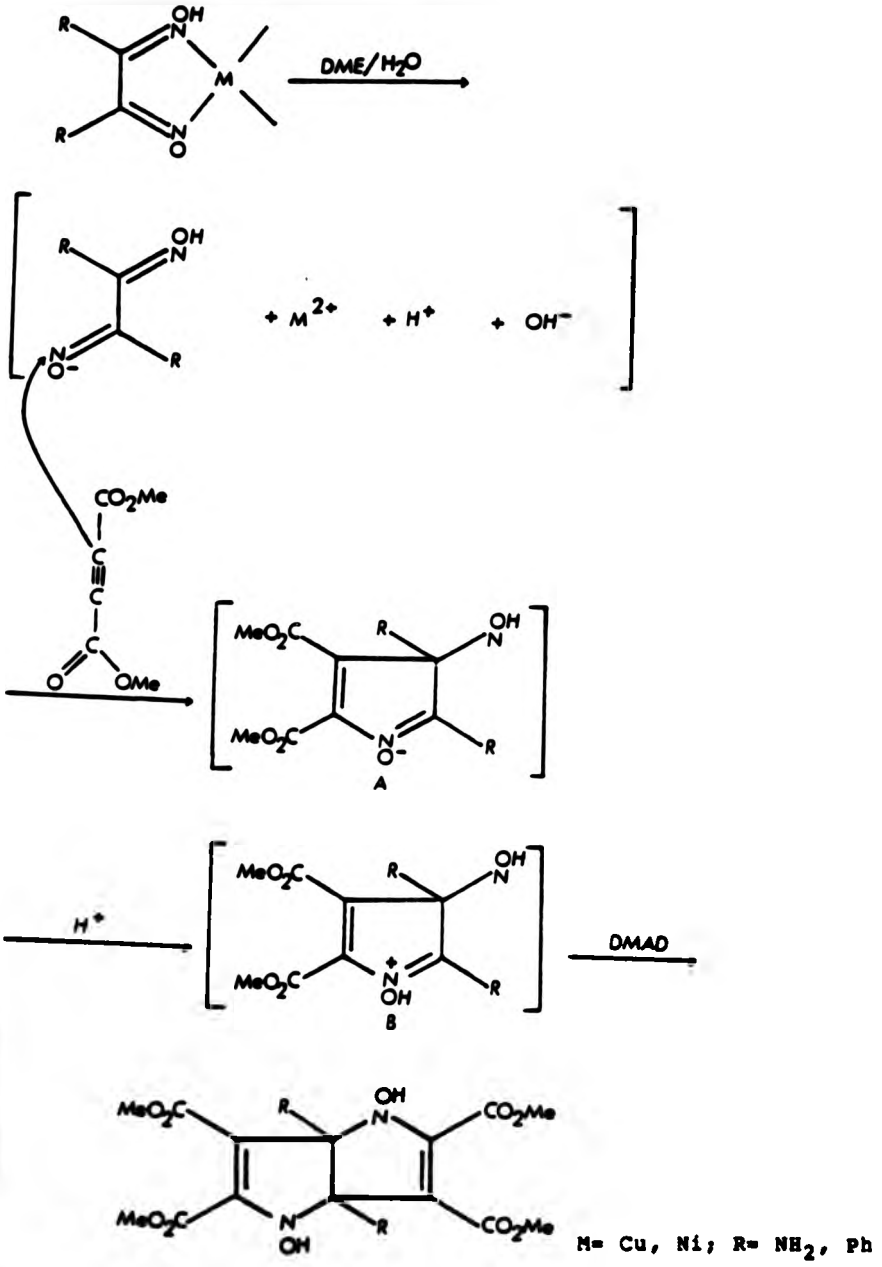


R= alkyl

2.43

A proposed mechanism for the formation of the 2:1 adducts arising from the reactions of the nickel(II) and copper(II) complexes of diaminoglyoxime and diphenylglyoxime with dimethyl acetyledicarboxylate is outlined in Scheme 2.12. One of the stages of the suggested mechanism involves attack of the electropositive site of the dipolarophile (DMAD) by the anionic oximic group of the ligand to give the intermediate A. This reacts further with a proton arising from the water present in the reaction system to give the intermediate B. Subsequently, the polarised oximic group encourages a 1,2-proton shift, leading to the formation of a 1,3-dipole. The occurrence of such intramolecular proton transfer, encouraged by the presence of a transition metal or transition metal complex, was discussed in Section 2.8.1. Attack of the electropositive site of another molecule of the dipolarophile by the nitrogen of the 1,3-dipole system leads to to the 2:1 cycloadduct C. The process also leads to the respective metal(II) hydroxide, which is not isolated in the pure state, as it hydrolyses dimethyl acetylene-dicarboxylate to give the metal(II) derivative of the carboxylate dianion 2.38.

In order to confirm the participation of water in these reactions, the behaviour of the copper(II) and nickel(II) glyoximato complexes with dimethyl acetylenedicarboxylate in dry 1,2-dimethoxyethane was examined. Both complexes failed to react with dimethyl acetylenedicarboxylate in the dry solvent, even after prolonged refluxing periods.



Scheme 2.12

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CHAPTER 3

3 Electron Impact and Chemical Ionisation Mass Spectra of Dioximes

3.1 Introduction

The electron impact (EI) mass spectra of various nitrogen-rich compounds, such as aromatic nitro compounds, have been extensively studied.[1-3] In general, these provide information about the molecular formula and fragmentation pathways of such compounds.

Positive ion chemical ionisation (PICI) mass spectrometry, a technique which involves the use of a reagent gas at relatively high pressures, has been extensively used for the detection of explosives and volatile constituents of explosives.[4-6] This mass spectrometric technique is particularly useful in studies of compounds in which the molecular ion is either very weak or completely absent from the corresponding electron impact mass spectra. Negative ion chemical ionisation (NICI) is a sensitive mass spectrometric technique, particularly useful in the study of explosives. In the negative ion mode, a compound under investigation may produce the corresponding molecular anion, due to electron capture.[7, 8] Alternatively, dissociative electron capture may occur from three-body ion/electron/molecule and ion/wall collisions, leading to anionic fragments and radicals.[8]

Another possibility in NICI mass spectromerty is ion-pair production. This type of behaviour is well established, and results in the formation of both anionic and cationic fragments. A number of explosives have been studied under chemical ionisation conditions, including 1,3,5-trinitrobenzene,[9] 2,4,6 N-tetranitro N-methylaniline,[9, 10] dynamite constituents nitroglycerine and ethylene glycol dinitrate,[11] and the military explosive 2,4,6-trinitrotoluene (TNT).[9, 10, 12] The importance of chemical ionisation mass spectrometric techniques in structure elucidation, which is not always possible with electron impact mass spectrometry, has resulted in enormous development of such techniques over the last few years.[13-17] The use of chemical ionisation in the study of oximic compounds has been very limited, with the chemical ionisation mass spectra of monooximes forming the bulk of such studies.[18]

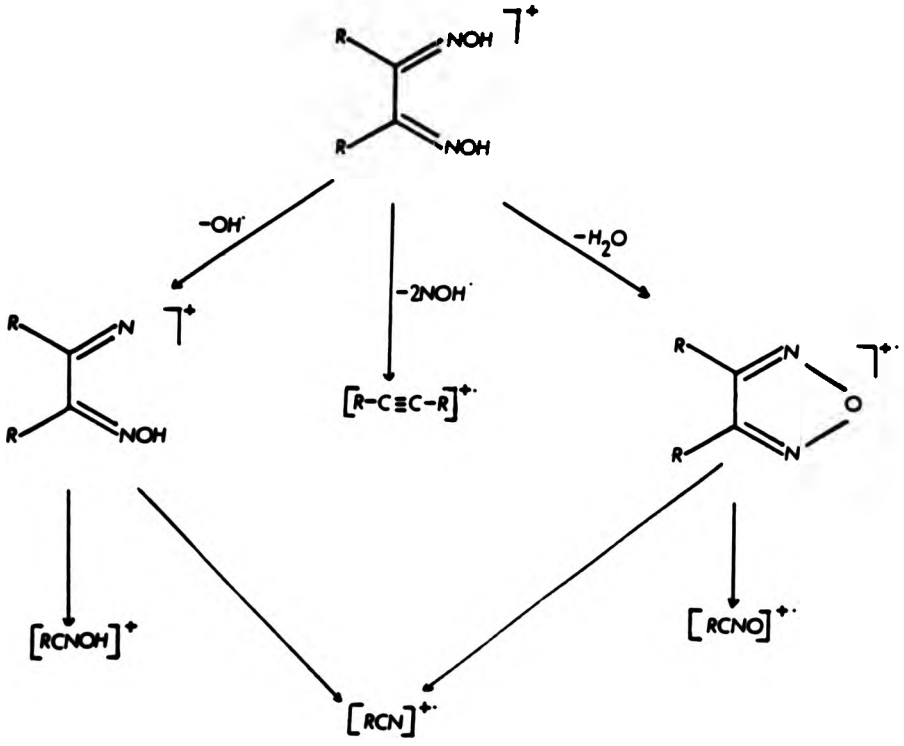
Electron impact (EI) mass spectrometric studies of vic-dioximes having simple alkyl or aryl substituents (e.g., H, Me, Ph), and their complexes have attracted some attention in the past.[19-23] Apart from a recent study on the NICI of dioximes with methyl and phenyl substituents,[19] the use of this method to examine vic-dioximes has received no attention.

3.2 Electron Impact and Chemical Ionisation Mass Spectra of Dioximes

Previous studies of the EI mass spectra of vic-dioximes, such as dimethylglyoxime ($dmgH_2$), and diphenylglyoxime ($dPhgH_2$), showed that such compounds give parent ions of moderate intensity.[20] A primary fragmentation pathway of the parent ion involves loss of hydroxyl radicals. Also, loss of water from the parent ion leads to furazan radical ions which fragment characteristically to give various other ions, such as $[CNO]^+$, $[CN]^+$, and $[NO]^+$. Another important process observed in the EI mass spectra of vic-dioximes is cleavage of the C-C bond. Deoximation also occurs to give ions of alkyne type. Generally, among the dioximes previously studied, no fragmentation leading to loss of the R substituent via cleavage of the R-C bond has been observed.[20] However, a recent report suggests that dimethylglyoxime fragments via loss of a methyl and a hydroxyl radical, but no accurate mass measurements are given to support this proposal.[21] The various fragmentation pathways are summarised in Scheme 3.1.

The PICI mass spectra of glyoxime, methylglyoxime, dimethylglyoxime, and diphenylglyoxime, in the presence of methane or ammonia at 0.5 torr, showed that these compounds display abundant $[M + H]^+$, and $[M]^{+\cdot}$ ions.[19] The NICI mass spectra of these dioximes, in the presence of ammonia,

exhibit peaks due to the ions $[M - H]^-$, and $[M - H_2O]^{-\cdot}$.[19]



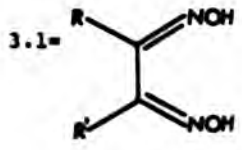
Scheme 3.1

The dioximes involved in the present mass spectrometric investigation are listed in Table 3.1. The cyclic dioxime 2,3-dioximino-piperazine (14) was also studied.

Table 3.1 Dioximes (3.1) Investigated Using Mass Spectrometric Techniques

Compound Number	R	R'
1	H	Cl
2	Cl	Cl
3	NH_2	NH_2
4	H	NH_2
5	NH_2	PhCN
6	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$
7	NH_2	$C_6H_2(NO_2)_3NH$
8	NH_2	$C_6H_3(NO_2)_2NH$
9	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$
10	H	tH
11	H	tCl
12	tH	tH
13	tCl	tCl

3.1=



Chloroglyoxime and Dichloroglyoxime

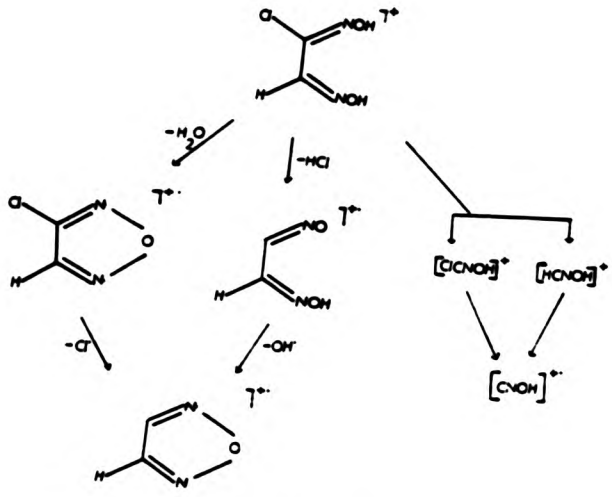
In both the EI mass spectra of anti-chloroglyoxime (1) and dichloroglyoxime (2), the parent ion peak is present, showing the appropriate isotopic pattern. In the case of anti-chloroglyoxime the parent ion peak is of moderate intensity, whereas in dichloroglyoxime this is of weak intensity (Table 3.2). Peaks due to ions arising from loss of $Cl^{\cdot}$ and HCl are present in both spectra. Although a peak due to loss of H_2O is absent in the spectrum of dichloroglyoxime, and of low intensity in the spectrum of chloroglyoxime, both spectra show peaks due to the ion $[M - H_2O - NO]^+$. Cleavage of the C-C bond occurs in both dioximes, as indicated by the presence of the ions $[ClC{=}NOH]^+$ (m/z= 78) in the mass spectra of both compounds, and $[HC{=}NOH]^+$ (m/z= 44) in the case of anti-chloroglyoxime. Furthermore, both compounds show peaks due to $[CNOH]^{+\cdot}$.

The presence of the C-Cl bond in these dioximes allows for decomposition reactions which are not observed in other dioximes. Thus, both compounds show peaks due to $[M - HCl - NO]^+$, $[M - Cl]^+$, and $[M - HCl]^{+\cdot}$. In the case of dichloroglyoxime, there is also an intense peak at m/z 84 which corresponds to a loss of two molecules of HCl from the parent ion. This fragmentation pathway probably leads to a furaxan N-oxide type ion. Other fragmentation pathways of these chloroglyoximes may also lead to furaxan ions as indicated in Schemes 3.2 and 3.3. The labile chloro-

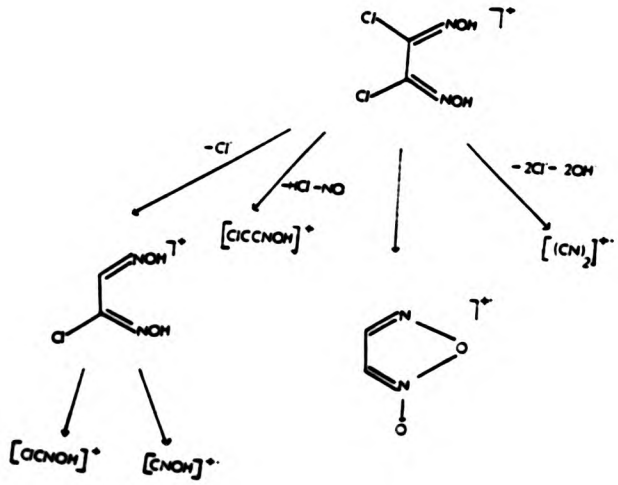
substituent is absent on the furaxan ions obtained from such fragmentations. This contrasts similar fragmentations of dioximes with non-labile substituents such as methyl and phenyl, and which lead to furaxan ions where the substituent is retained.[20, 23] Also, in contrast to dioximes with non-labile substituents, the EI mass spectra of dichloroglyoxime and anti-chloroglyoxime show no ions corresponding to $[Cl-C{\equiv}C-Cl]^{+\cdot}$, and $[Cl-C{\equiv}C-H]^{+\cdot}$, respectively.

Table 3.2 Ion Abundances in the EI Mass Spectra of the Chloroglyoximes

Chloroglyoxime		Dichloroglyoxime		
m/z	Intensity (%)	m/z	Intensity (%)	Assignment
122/124	22/6	156/158	3/2	$[M]^{+\cdot}$
104/106	11/3	---	---	$[M - H_2O]^{+\cdot}$
87	40	121/123	13/4	$[M - Cl]^{+}$
86	41	120/122	5/2	$[M - HCl]^{+\cdot}$
78/80	8/2	78/80	4/1	$[ClC{=}NOH]^{+}$
74/76	19/6	108/110	1/1	$[M - H_2O - NO]^{+}$
69	8	69	2	$[HC{=}N(O)N{=}C]^{+}$
68	2	68	2	$[C{=}N(O)N{=}C]^{+\cdot}$
56	10	90/92	8/2	$[M - HCl - NO]^{+}$
---	---	84	53	$[M - 2HCl]^{+\cdot}$
44	39	---	---	$[HC{=}NOH]^{+}$
43	28	43	5	$[CNOH]^{+\cdot}$



Scheme 3.2



Scheme 3.3

The effect of the chloro-substituent on the fragmentation pattern of these dioximes is also evident from the methane NICI mass spectrum of anti-chloroglyoxime (Figure 3.1). This shows the $[M - H]^-$ ion as the highest m/z ion with the appropriate isotopic patterns. The absence of $[M]^{-\cdot}$ in the methane NICI mass spectrum of anti-chloroglyoxime is in line with the behaviour of other dioximes under negative chemical ionisation conditions.[19] Also present are prominent peaks due to ions arising by decomposition involving loss of O at m/z 105/103, and loss of HCl at m/z 85. The base peak in this spectrum is at m/z 69, and is due to $[M - HCl - OH]^-$. Subsequent fragmentations of this ion involves loss of $H^\cdot$ radicals, and HCN, and gives rise to peaks at m/z 68 and 42, respectively. The spectrum shows peaks at m/z 52 and 54, which exhibit the isotopic pattern expected for one chlorine, and most probably corresponds to $[HClO]^{-\cdot}$. A peak due to $[Cl]^-$ is also present.

The methane NICI mass spectrum of dichloroglyoxime shows some close similarities to that of anti-chloroglyoxime, but also some notable differences (Figure 3.2). The spectrum shows a fairly intense peak due to $[M - H]^-$ and ions arising by loss of HCl from $[M - H]^-$ and subsequent loss of O. Resemblances are also apparent with regard to the absence of a peak due to $[M]^{-\cdot}$, and the presence of a peak due to $[HClO]^{-\cdot}$. Special features observed in the methane NICI spectrum of dichloroglyoxime is the presence of intense peaks corresponding to $[M + Cl]^-$ and of peaks assignable to

the ion $[HCl_2]^-$. Such ions are not unusual in the NICI spectra of haloganated compounds, which may yield negative halogen ions $[X]^-$, that in turn collide with neutral molecules to give species of the type $[M + X]^-$.[24, 25]

For dichloroglyoxime, it was also possible to record its PICI mass spectrum using isobutane as the reactant gas. The spectrum exhibits the $[M + H]^+$ ion as the base peak, and a peak of a very weak intensity due to $[M]^{+\cdot}$. A complex pattern of prominent peaks at m/z 121, 123, 125, and 127 corresponding to ions arising by losses of HCl and $Cl^\cdot$ from $[M + H]^+$ are present. Other prominent peaks appear at m/z 84 and 85, and correspond to the ions $[M - 2HCl]^{+\cdot}$ and $[M - HCl - Cl]^+$, respectively.

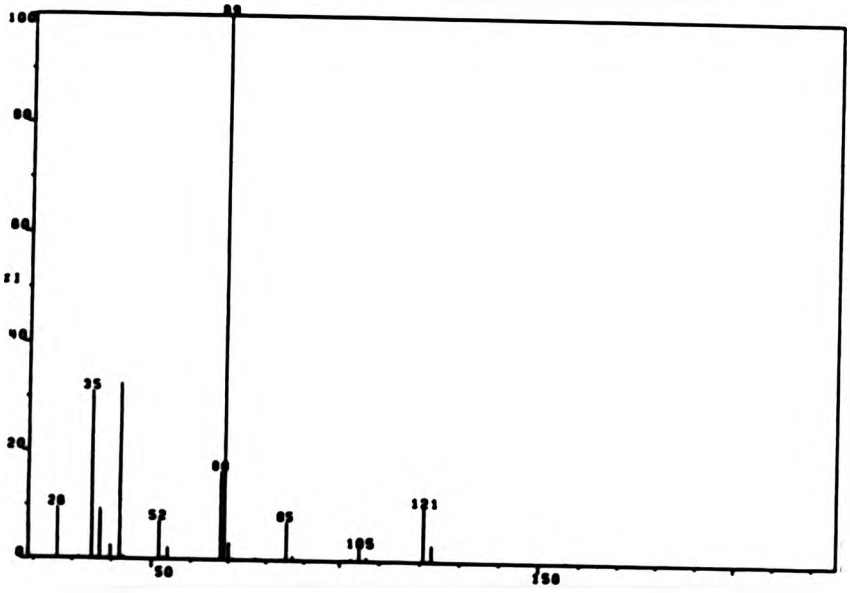


Figure 3.1 Methane NICI Mass Spectrum of anti-Chloroglyoxime

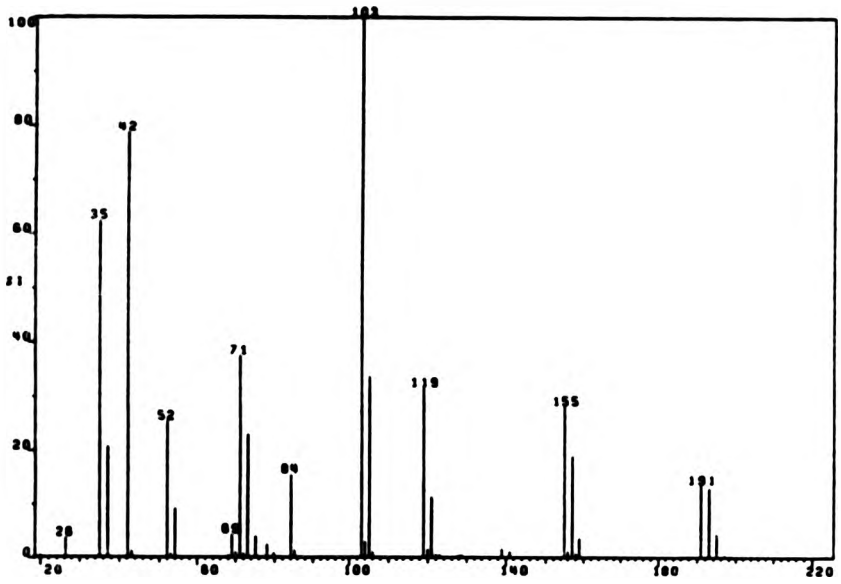


Figure 3.2 Methane NICI Mass Spectrum of Dichloroglyoxime

Aminoglyoxime and Diaminoglyoxime

The EI mass spectrum of diaminoglyoxime (3) has been reported earlier.[23] This study demonstrated that fragmentation of the parent ion involves loss of $OH^{\bullet}$, and H_2O, to give peaks of very weak intensity. Cleavage of the C-C bond also occurs leading to a peak of moderate intensity assignable to $[H_2NCNOH]^+$. As noted earlier, such fragmentation pathways are typical of most dioximes (Scheme 3.1). In addition, a peak of weak intensity at m/z 102 was previously attributed to the loss of O.

The present study generally confirms the results previously obtained, and most of the proposed ion assignments (Table 3.3). The ion at m/z 102 can arise either by loss of O or $NH_2^{\cdot}$ from the parent ion. The weak N-O bond makes the former cleavage more probable than the latter. Accurate mass measurements made during the present study confirm that the ion at m/z 102 is predominantly due to the loss of O from the parent ion, rather than loss of $NH_2^{\cdot}$. Loss of O from the parent ion leads to the fragment of elemental composition $[C_2H_6N_4O]^{+\cdot}$, whereas loss of $NH_2^{\cdot}$ leads to the fragment of elemental composition $[C_2H_4N_3O_2]^{+\cdot}$, and the contribution of these to the peak at m/z 102 is in the ratio 77:23%, respectively. However, in contrast to the previous report, the peak at m/z 88, previously attributed to loss of $(NH)_2$, is now attributed to loss of $NO^{\cdot}$. Elimination of $(NH)_2$ from diaminoglyoxime seems to be a drastic change, but loss of $NO^{\cdot}$ is more reasonable. In addition, accurate mass measurements indicate that the ion at m/z 88 has the elemental composition $[C_2H_6N_3O]^{+}$, which confirms the above suggestion. The presence of a peak at m/z 30 due to $[NO]^{+}$ has been previously observed in the mass spectra of chemically related compounds such as furoxans and furazans.[26, 27]. The base peak in the EI spectrum of diaminoglyoxime is at m/z 43. Accurate mass measurements indicate that this peak is due to the ion $[H_2NC{=}NH]^{+\cdot}$, which arises from cleavage of the C-C bond, and loss of O from the resulting radical ion. The moderate peak at m/z 59 was previously assigned to the ion $[H_2NCNOH]^{+}$.[23] The presence of the ion $[H_2NCNOH]^{+}$ in the EI

spectrum of diaminoglyoxime is analogous to the behaviour of the chloroglyoximes, which exhibit the ions $[ClCNOH]^+$. Although a peak due to $[M - OH]^+$ is absent and the peak due to $[M - H_2O]^{+\cdot}$ is of weak intensity, there are peaks due to $[M - H_2O - NO]^+$ and $[M - OH - NO]^{+\cdot}$.

The EI mass spectrum of aminoglyoxime (4) shows a parent ion peak of moderate intensity at m/z 103 (Table 3.3), which fragments in a similar way to that of diaminoglyoxime and other dioximes with non-labile substituents. Thus, this spectrum exhibits ions due to loss of O, $OH^{\cdot}$, and H_2O. In contrast to diaminoglyoxime, the loss of O is very pronounced and leads to the base peak. Loss of $NO^{\cdot}$ also occurs in the compound. Peaks at m/z 56 and 55 are present due to $[M - OH - NO]^{+\cdot}$ and $[M - H_2O - NO]^+$, respectively.

The presence of a peak due to the ion $[H_2NC{=}NH]^+$, and the accurate mass measurements which show thal loss of $NH_2^{\cdot}$ from the parent ion of diaminoglyoxime is unfavourable, indicate the strength of the amino-carbon ($C-NH_2$) bond. This is in contrast to the behaviour of the chloroglyoximes, the EI spectra of which contain peaks due to ions arising by loss of $Cl^{\cdot}$.

Table 3.3 Ion Abundances in the EI Mass Spectra of the Aminoglyoximes

Aminoglyoxime		Diaminoglyoxime		
m/z	Intensity (%)	m/z	Intensity (%)	Assignment
103	33	118	68	$[M]^{+\cdot}$
87	100	102	1	$[M - O]^{+\cdot}$
86	8	---	---	$[M - OH]^{+}$
85	3	100	1	$[M - H_2O]^{+\cdot}$
73	28	88	16	$[M - NO]^{+}$
---	---	59	20	$[H_2NC{=}NOH]^{+}$
---	---	43	100	$[H_2NC{=}NH]^{+}$
56	9	71	11	$[M - OH - NO]^{+\cdot}$
55	9	70	5	$[M - H_2O - NO]^{+}$

During this study, the behaviour of diaminoglyoxime in the mass spectrometer was also investigated under both positive and negative ion chemical ionisation conditions.

The methane NICI spectrum of diaminoglyoxime shows an intense peak at m/z 117 due to $[M - H]^-$ (Table 3.4). The main fragmentation pathway involves cleavage of the C-C bond and leads to the ions $[HNCNOH]^{-\cdot}$, $[HNCNO]^-$, $[HNCN]^-$, and $[CN]^-$. Loss of $OH^\cdot$ from $[M - H]^-$ occurs as indicated by a peak of weak intensity at m/z 100, and is followed by loss of O and $NO^\cdot$. Fragmentation involving cleavage of the C-C bond also occurs, and leads to a peak of weak intensity corresponding to $[H_2NC{=}NO]^{-\cdot}$. Significantly, peaks corresponding to

fragments arising from deoximation of the dioxime are absent.

Table 3.4 Ion Abundances in the Methane NICI Mass Spectrum of Diaminoglyoxime

m/z	Intensity (%)	Assignment
118	3	$[M]^{-\cdot}$
117	73	$[M - H]^-$
100	1	$[M - H - OH]^{-\cdot}$
84	14	$[M - 2OH]^{-\cdot}$
70	11	$[M - H_2O - NO]^-$
68	32	$[H_2N(CN)_2]^-$
58	6	$[HNCNOH]^{-\cdot}$
57	4	$[HNCNO]^-$
41	100	$[HNCN]^-$
26	16	$[CN]^-$

The base peak in the isobutane PICI mass spectrum of diaminoglyoxime is at m/z 119 and corresponds to the $[M + H]^+$ ion, whereas the peak corresponding to the parent ion $[M]^{+\cdot}$ is of low intensity (Figure 3.3, Table 3.5). This spectrum also shows peaks analogous to peaks obtained in the EI spectrum of the dioxime, such as peaks due to $[(M + H) - O]^+$, and $[M - H_2O - NO]^+$. In addition, a peak of strong intensity appears at m/z 87, and most probably corresponds to the ion $[(M + H) - 2O]^+$. Also present in the isobutane PICI spectrum of this compound is a peak at m/z 161, which possibly arises from a collision process

involving neutral diaminoglyoxime and the ion $[CNOH]^{+\cdot}$. Equally likely, is the formation of this ion from collision of neutral diaminoglyoxime with $[C_3H_7]^{+\cdot}$ which arises from the fragmentation of isobutane.

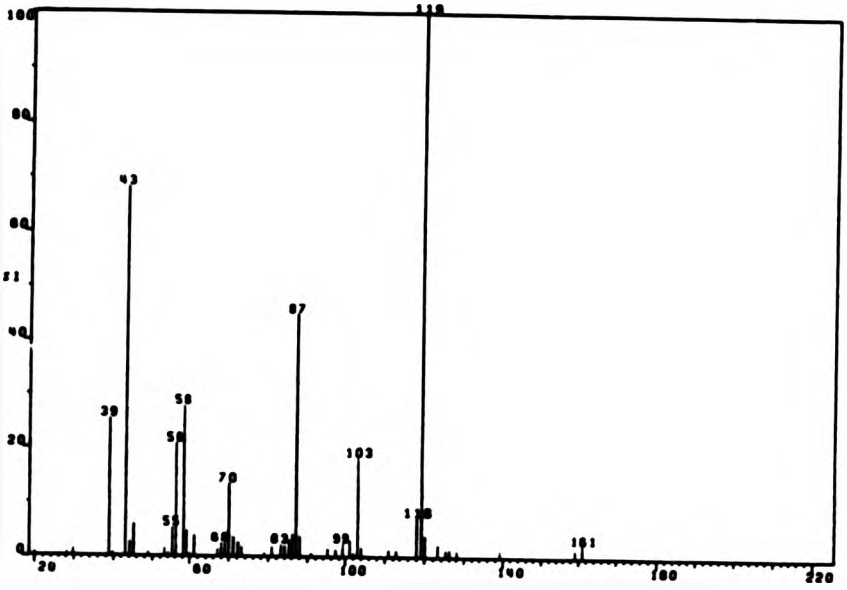


Figure 3.3 Isobutane PICI Mass Spectrum of Diaminoglyoxime

Table 3.5 Ion Abundances in the Isobutane PICI Mass Spectrum of Diaminoglyoxime

m/z	Intensity (%)	Assignment
161	2	$[M + H_2NC{=}NH]^+$
119	100	$[M + H]^+$
118	7	$[M]^{+\cdot}$
103	18	$[(M + H) - O]^+$
87	44	$[(M + H) - 2O]^+$
70	13	$[M - H_2O - NO]^+$

1-Amino-2-(benzyl-N-imino)glyoxime

In line with other dioximes, 1-amino-2-(benzyl-N-imino)-glyoxime (5) shows the usual losses of OH·, and H_2O from the parent ion in its EI mass spectrum (Figure 3.4, Table 3.6). However, no deoximation or C-C cleavage reactions are observed. A notable feature of the decomposition of the parent ion in the EI spectrum of this compound is the successive losses of two hydrogens. This leads to a peak of moderate intensity at m/z 204 due to $[M - 2H]^{+\cdot}$. A probable formulation for this ion is 3.2, which is formed by a rearrangement process (Scheme 3.4). This is in contrast to the behaviour of 1-amino-2-(2-hydroxybenzyl-N-imino)glyoxime, which shows no such losses, presumably because such a rearrangement is rendered unfavourable due to the presence of the hydroxyl group (Chapter 2, 2.19).[23] The base peak in the EI spectrum of 1-amino-2-(benzyl-N-imino)glyoxime appears at m/z 105, and exact mass measurements indicate that this ion has the elemental composition $[C_6H_5CO]^+$ rather than $[C_6H_5CNH_2]^+$. The formation of this ion can be readily accounted in terms of the suggested formulation of the ion $[M - 2H]^{+\cdot}$. Fragmentation involving the formation of the benzoyl cation $[C_6H_5CO]^+$ has been found to occur in the mass spectra of 2,2-diphenyl-3-arylcyclobutanone oximes.[28]

In the isobutane PICI and methane NICI spectra of 1-amino-2-(benzyl-N-imino)glyoxime there are peaks of strong intensity due to the ions $[M + H]^+$ and $[M - H]^-$, respectively

(Tables 3.7 and 3.8). The fragmentation of these ions involve loss of H•, OH•, and H_2O.

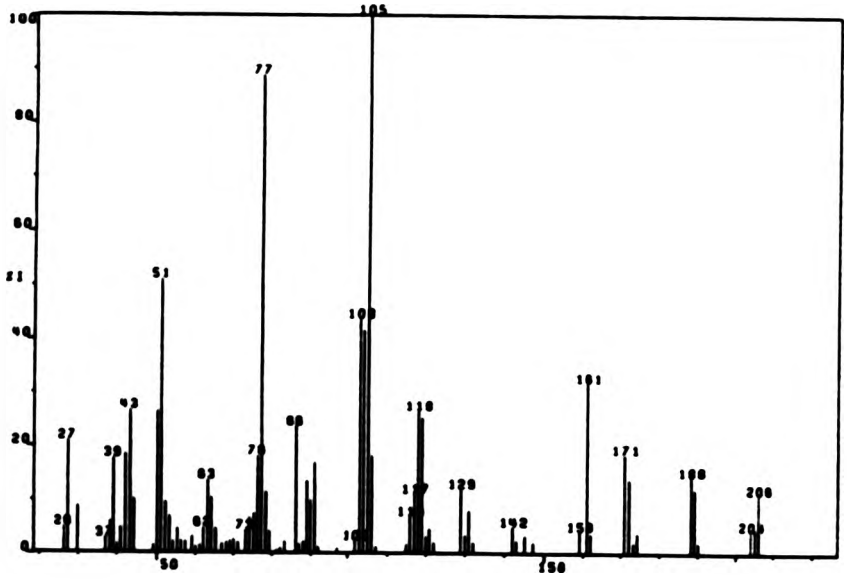
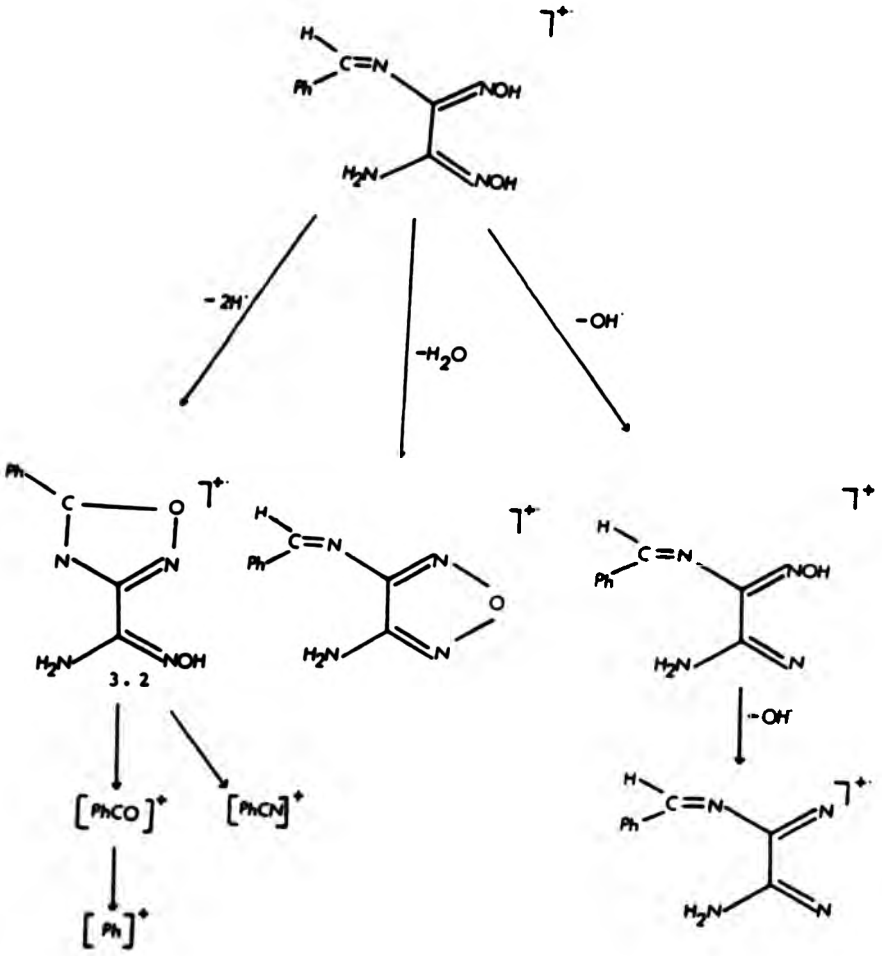


Figure 3.4 EI Mass Spectrum of 1-Amino-2-(benzyl-N-imino)-glyoxime

Table 3.6 Ion Abundances in the EI Mass Spectrum of 1-Amino-2-(benzyl-N-imino)glyoxime

m/z	Intensity (%)	Assignment
206	11	$[M]^{+\cdot}$
205	4	$[M - H]^{+}$
204	4	$[M - 2H]^{+\cdot}$
189	12	$[M - OH]^{+}$
188	14	$[M - H_2O]^{+\cdot}$
172	14	$[M - 2OH]^{+\cdot}$
161	32	$[M - H_2O - HCN]^{+\cdot}$
106	18	$[C_6H_5CHO]^{+\cdot}$
105	100	$[C_6H_5CO]^{+}$
103	44	$[C_6H_5CN]^{+\cdot}$
77	89	$[C_6H_5]^{+}$
43	27	$[HCNO]^{+\cdot}$
27	21	$[HCN]^{+\cdot}$



Scheme 3.4

Table 3.7 Ion Abundances in the Isobutane PICI Mass Spectrum of 1-Amino-2-(benzyl-N-imino)glyoxime

m/z	Intensity (%)	Assignment
207	100	$[M + H]^+$
191	33	$[(M + H) - O]^+$
189	44	$[(M + H) - H_2O]^+$
173	30	$[(M + H) - 2OH]^+$
162	11	$[(M + H) - H_2O - HCN]^+$

Table 3.8 Ion Abundances in the Methane NICI Mass Spectrum of 1-Amino-2-(benzyl-N-imino)glyoxime

m/z	Intensity (%)	Assignment
206	2	$[M]^{-\cdot}$
205	19	$[M - H]^-$
189	7	$[M - OH]^-$
188	11	$[M - H_2O]^{-\cdot}$
187	31	$[(M - H) - H_2O]^-$
169	10	$[M - H - 2H_2O]^-$
146	11	$[C_6H_5CHNCNO]^{-\cdot}$
145	100	$[C_6H_5CNCNO]^-$
131	18	$[C_6H_5CHNCNH]^-$
83	12	$[M - C_6H_5CO - H_2O]^-$
41	18	$[HNCN]^-$
26	4	$[CN]^-$

Dioximes with Polynitroaromatic Substituents

The EI, isobutane PICI, and methane NICI mass spectra of the dioximes 1,2-di(2,4,6-trinitrophenyl-N-amino)glyoxime (6), 1-amino-2-(2,4,6-trinitrophenyl-N-amino)glyoxime (7), 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (8), and 1,2-di(3-nitrophenyl-N-amino)glyoxime (9) were investigated. Increasing number of nitro groups reduce the stability of the neutral ions. Thus, in the EI spectrum of 1,2-di(3-nitrophenyl-N-amino)glyoxime the parent ion peak at m/z 360 is of moderate intensity, whereas in the case of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime the parent ion peak at m/z 284 is of weak intensity. However, the dioximes with trinitroaromatic substituents show no parent ion peaks. This observation is in accordance to the thermal properties of these dioximes, which show that additional number of nitro groups tend to lower the decomposition temperature of these dioximes (Chapter 4). The instability of the molecule and of the molecular ion with increasing number of nitro groups has been previously discussed for nitrobenzenes,[29] and 1-phenyl-3-nitrophenyl-2-pyrazolines.[30]

The mass spectra of all four dioximes show peaks due to ions arising from successive losses of OH· and NO· from the respective parent ions. Among the common features of the EI spectra of all dioximes with nitroaromatic substituents are processes involving cleavage of the R-C bond (R= nitroaromatic substituent). In all cases loss of O from

the nitro-substituents occurs. Loss of oxygen is a common process in the fragmentation pattern of nitroaromatic compounds.[2] The peak due to ion $[C_6H_5NO]^{+\cdot}$ is present with high intensity in all spectra. Also, the ions $[NO_2]^+$ and $[NO]^+$ are highly abundant on the mass spectra of all the dioximes with polynitroaromatic substituents. Fragmentation through loss of $NO^{\cdot}$ is also shown by ions involved in the fragmentation of these compounds. This type of behaviour is very characteristic in the EI spectra of nitroaromatic compounds. A previous report suggests that in such reactions, a nitro to nitrite isomerisation is involved before decomposition.[31] Assignment of peaks due to low mass fragments in the spectra of dioximes with polynitro aromatic substituents obtained under chemical ionisation conditions cannot be made, because of the possibility of different reactions occuring within the CI ion source. For example, previous reports suggest that the nitro group may be reduced to the corresponding amine group within the CI ion source.[32, 33]

Among the EI mass spectra of the four dioximes with polynitroaromatic substituents, only that of 1,2-di(3-nitrophenyl-N-amino)glyoxime shows losses from the parent ion analogous to those found in other dioximes (Table 3.9). These include losses such as $2OH^{\cdot}$, and H_2O. Also present are peaks due to deoximation and C-C cleavage reactions. Subsequent reactions after C-C cleavage lead to the ion $[RCN]^{+\cdot}$. The EI of this compound also shows fragmentation

pathways characteristic of aromatic nitro compounds. For example, peaks arising from the ions $[M - OH - NO]^{+\cdot}$, and $[M - H_2O - NO]^{+}$ are present.

Table 3.9 Ion Abundances in the EI Mass Spectrum of 1,2-Di(3-nitrophenyl-N-amino)glyoxime

m/z	Intensity (%)	Assignment
360	10	$[M]^{+\cdot}$
344	3	$[M - O]^{+\cdot}$
342	21	$[M - H_2O]^{+\cdot}$
329	10	$[M - NOH]^{+\cdot}$
326	47	$[M - 2OH]^{+\cdot}$
312	10	$[M - OH - NO]^{+\cdot}$
311	15	$[M - H_2O - NO]^{+}$
279	29	$[M - 2OH - HNO_2]^{+\cdot}$
180	15	$[R\text{-}CNOH]^{+}$
164	84	$[C_6H_4NONHCNOH]^{+}$
163	61	$[C_6H_4NO_2NHCN]^{+\cdot}$
149	57	$[C_6H_4NONHCNH_2]^{+\cdot}$
138	32	$[C_6H_4NO_2NH_2]^{+\cdot}$
118	52	$[C_6H_5NHC\ N]^{+\cdot}$
90	100	$[O_2NCHNOH]^{+\cdot}$

The fragmentation pattern in the isobutane PICI mass spectrum of 1,2-di(3-nitrophenyl-N-amino)glyoxime shows a peak of strong intensity due to the ion $[M + H]^{+}$, and similar fragmentation pathways to those obtained in its EI spectrum

(Table 3.10). The base peak in this spectrum appears at m/z 181 and arises from C-C cleavage of the $[M + H]^+$ ion. A peak of moderate intensity at m/z 139 is attributed to the ion $[nitroaniline + H]^+$. The methane NICI spectrum of 1,2-di(3-nitrophenyl-N-amino)glyoxime shows no peak due to the ion $[M - H]^-$, and little fragmentation. The base peak is at m/z 325 and is most probably due to the ion $[(M - H) - 2OH]^-$.

Table 3.10 Ion Abundances in the Isobutane PICI Mass Spectrum of 1,2-Di(3-nitrophenyl-N-amino)glyoxime

m/z	Intensity (%)	Assignment
361	35	$[M + H]^+$
345	32	$[(M + H) - O]^+$
344	7	$[(M + H) - OH]^{+\cdot}$
343	32	$[(M + H) - H_2O]^+$
330	27	$[(M + H) - HNO]^+$
329	82	$[(M + H) - 2O]^+$
328	26	$[(M + H) - O - OH]^{+\cdot}$
327	84	$[(M + H) - 2OH]^+$
181	100	$[RCNOH + H]^{+\cdot}$
180	15	$[RCNOH]^+$
164	69	$[RCNH]^+$
138	13	$[C_6H_4(NO_2)NH_2]^{+\cdot}$

The predominant fragmentation pattern in the EI spectrum of

1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime is cleavage of the R-C bond with subsequent fragmentation of the nitroanilino ion. The isobutane PICI spectrum of this dioxime shows a peak due to $[M + H]^+$ of moderate intensity (Figure 3.5). Like the EI spectrum of the compound, this does not show the usual losses such as O, $OH^{\cdot}$, H_2O, typical of dioximes, but the main peaks observed are due to ions involving the decomposition of the dinitroanilino ion. The base peak in this spectrum is at m/z 103, and probably arises from loss of the dinitroaromatic substituent, which gives rise to the ion $[(M + H) - R]^+$. The methane NICI spectrum of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime does not show a peak due to $[M - H]^-$, but the highest peak appears at m/z 183 which is probably due to the dinitroaniline ion $[C_6H_3(NO_2)_2NH_2]^{-\cdot}$. This fragments further by loss of $NH_2^{\cdot}$ to give the base peak at m/z 167, which fragments further by loss of $NO^{\cdot}$ to give a peak of strong intensity at m/z 137.

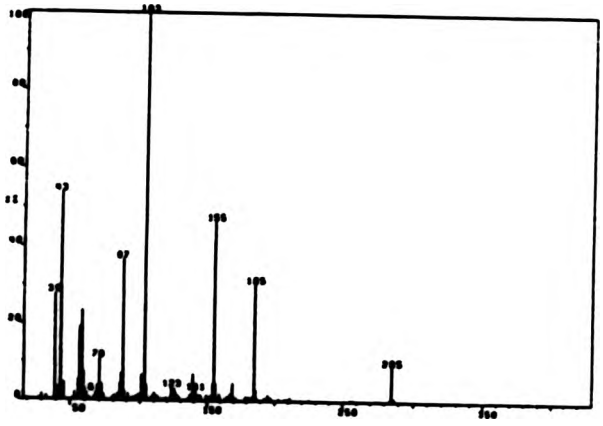


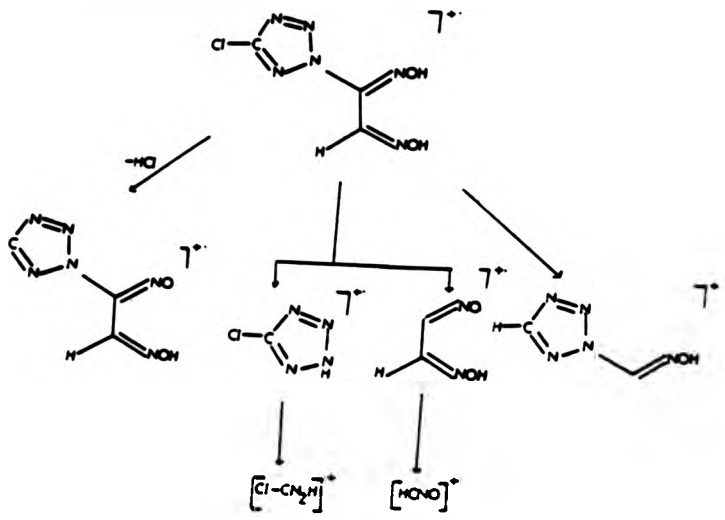
Figure 3.5 Isobutane PICI Mass Spectrum of 1-Amino-(2,4-dinitrophenyl-N-amino)glyoxime

Tetrazolyl-substituted dioximes

The dioximes with the tetrazolyl substitutents examined are 1-(5-tetrazolato)glyoxime (10), 1-(5-chlorotetrazolato)-glyoxime (11), 1,2-di(tetrazolato)glyoxime (12), and 1,2-di(5-chlorotetrazolato)glyoxime (13). Characteristic fragmentation modes of tetrazoles,[34] as well as of dioximes are present.[20]

Under EI conditions, the mass spectra of these dioximes do not exhibit a parent ion peak. The EI mass spectra of this class of dioximes indicate that they undergo decomposition prior to ionisation. The EI spectrum of 1-(5-chloro-tetrazolato)glyoxime does not exhibit the parent ion peak, but shows a fairly intense peak due to the ion $[M - HCl]^{+\cdot}$. Fragment ions arising by cleavage of the C-C bond and subsequent rapture of the tetrazolyl ring are also present (Scheme 3.5).

The EI mass spectrum of 1-(5-tetrazolato)glyoxime does not show a peak due to the parent ion, but the peak of the highest m/z value appears at 128, and probably arises from loss of N_2 from the parent ion. This spectrum also includes a peak of high intensity at m/z 129, which arises by loss of HCN from the parent ion.



Scheme 3.5

The isobutane PICI mass spectrum of 1,2-di(5-tetrazolato)-glyoxime shows fragmentation pathways typical of dioximes and 2,5-disubstituted tetrazolato compounds (Table 3.11). This spectrum gives a peak of moderate intensity at m/z 225 due to $[M + H]^+$. Furthermore peaks of moderate intensity due to the ions $[(M + H) - O]^+$, $[(M + H) - N_2]^+$, $[(M + H) - NOH]^+$, and $[(M + H) - 2N_2]^+$, are present. The base peak in this spectrum is at m/z 154, and arises by loss of one tetrazolyl substituent from the parent ion to give a

peak due to the fragment $[M - HtH]^{+\cdot}$.

The isobutane PICI spectrum of 1,2-di(5-chlorotetrazolato)-glyoxime shows a peak of moderate intensity due to $[M + H]^+$, with the appropriate isotopic pattern. Loss of N_2 from $[M + H]^+$ is evident by peaks of weak intensity at m/z 265/267. The base peak appears at m/z 105, and is due to the ion $[5\text{-chlorotetrazole} + H]^+$.

Table 3.11 Ion Abundances in the Isobutane PICI Mass Spectrum of 1,2-Di(5-tetrazolato)glyoxime

m/z	Intensity (%)	Assignment
225	4	$[M + H]^+$
209	8	$[(M + H) - O]^+$
197	11	$[(M + H) - N_2]^+$
194	10	$[(M + H) - NOH]^+$
182	38	$[(M + H) - O - HCN]^+$
169	54	$[(M + H) - 2N_2]^+$
154	100	$[M - HtH]^{+\cdot}$
139	21	$[M - tH - O]^{+\cdot}$
111	24	$[Ht\text{-}C{=}NO]^{+\cdot}$
71	36	$[HtH + H]^+$

A common fragmentation pathway shown in the isobutane PICI spectra by all these dioximes is the loss of the corresponding tetrazolyl radical $[HtX - H]^{+\cdot}$, or the cation

of the protonated tetrazole molecule $[HtX]^+$. The most significant feature in the isobutane PICI mass spectra of 1,2-di(5-tetrazolato)glyoxime, and 1,2-di(5-chloro-tetrazolato)glyoxime is loss of N_2 and $2N_2$ from the respective $[M + H]^+$ ions. The loss of N_2 from $[(M + H) - R]^{+\cdot}$ and $[(M + H) - HR]^+$ is equally important in the both spectra (Table 3.12). Such losses also occur in the isobutane PICI and methane NICI spectra of the dioximes with only one tetrazolyl substituent (10 and 11).

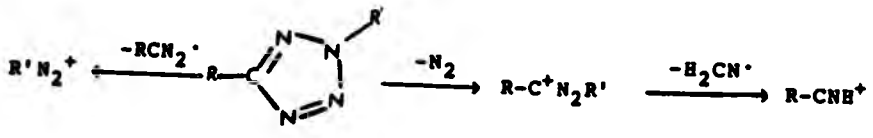
Table 3.12 Important Fragments in the Isobutane PICI Mass Spectra of 1,2-di(5-tetrazolato)glyoxime, and 1,2-di(5-chlorotetrazolato)glyoxime

	1,2-di(5-tetrazolato)-glyoxime	1,2-di(5-chloro-tetrazolato)glyoxime
	m/z (%)	m/z (%)
$[M + H]^+$	225 (2)	293 (30)/ 295 (20)
$[(M + H) - N_2]^+$	197 (11)	265 (5)/ 267 (3)
$[(M + H) - 2N_2]^+$	169 (54)	237 (low)
$[(M + H) - R - N_2]^{+\cdot}$	128 (13)	162 (4)/ 164 (1)
$[(M + H) - HR - N_2]^+$	127 (5)	161 (24)/ 163 (7)

In the past, mass spectrometry has been used to distinguish between the 2,5-disubstituted tetrazole structure and the isomeric 1,5-disubstituted structure.[35-37] The fragmentation pattern of 2,5-disubstituted tetrazoles involves loss of N_2

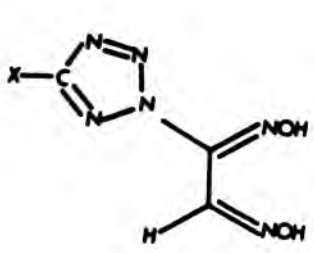
and a subsequent loss of a hydrogen atom. The ion formed then loses HCN (Scheme 3.6). In contrast, the fragmentation pattern for 1,5-disubstituted tetrazoles is more complicated. In general, these involve loss of $RCN_2^{\cdot}$, but may vary considerably with the nature of the tetrazole ring substituents.[34] No explanation has yet been suggested for any relation of these mass spectral fragmentations with the disubstituted tetrazole structure.

The fragmentation pattern of the dioximes with tetrazolyl substituents which include losses of N_2, and HCN from their respective $[M + H]^+$ ions, suggest that bonding of the tetrazole ring in these compounds occurs through the N(2) site (3.3 and 3.4). This is supported by the absence of any peaks due to loss of $RCN_2^{\cdot}$ in these mass spectra, typical of 1,5-disubstituted tetrazoles.



R= e.g., H, Me; R'= e.g., Me

Scheme 3.6



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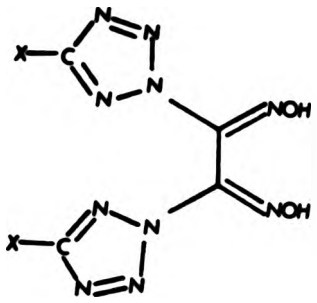

3.4

In the case of 1-(5-tetrazolato)glyoxime, its methane NICI spectrum shows a peak of moderate intensity due to $[M - H]^-$ (Figure 3.6). Reactions involving loss of O, and NO· from $[M - H]^-$ are also indicated by peaks at m/z 139, and 125, respectively. This spectrum also shows a peak at m/z 112 which arises from cleavage of the C-C bond to give the ion $[HtCNOH]^-$. This ion fragments further by loss of N_2 and O, as shown by the peaks of strong intensity at m/z 84 and 96, respectively. The base peak appears at m/z 69, and corresponds to the tetrazolyl ring ion $[tH]^{-}\cdot$. This subsequently fragments in a manner typical of 2,5-disubstituted tetrazoles.[35]

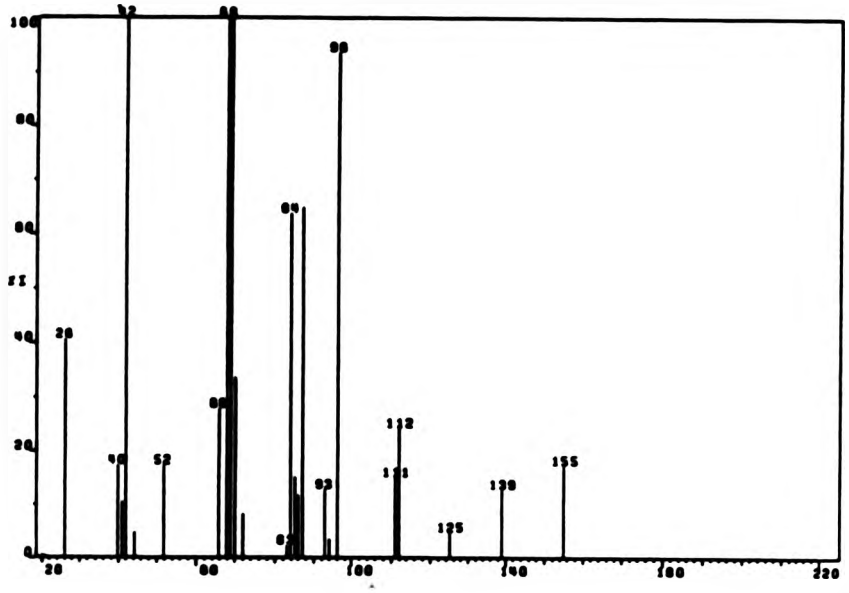

Figure 3.6 Methane NICI Mass Spectrum of 1-(5-Tetrazolato)-glyoxime

The methane NICI spectrum of 1-(5-chlorotetrazolato)glyoxime displays a peak due to $[M - H]^-$. This ion shows some reactions typical of many dioximes, such as losses of O and H_2O. A peak at m/z 155 probably arises from loss of $Cl^\cdot$ from $[M]^{-\cdot}$, and is due to $[M - Cl]^-$. The base peak in this spectrum is at m/z 103, and corresponds to the 5-chlorotetrazolyl ion $[tCl]^{-\cdot}$.

2,3-Dioximino-piperazine

For the dioxime 2,3-dioximino-piperazine (14), its mass spectrum was studied both under EI, and PICI conditions (Tables 3.13 and 3.14). This heterocyclic dioxime suffered more extensive fragmentation compared to the previously discussed dioximes.

The EI mass spectrum of 2,3-dioximino-piperazine exhibits a weak parent ion peak at m/z 144, which shows the typical loss of H_2O to give a furaxan type ion, shown by most vic-dioximes. Also present are peaks arising from losses of O, OH·, and NO· leading to ions such as $[M - O]^{+\cdot}$, $[M - OH]^{+}$, and $[M - NO]^{+}$. Deoximation of the parent ion leads to the ions $[M - NOH]^{+\cdot}$, and $[M - 2NOH]^{+\cdot}$. The latter corresponds to the [piperazine - 2H]$^{+\cdot}$ ion and fragments by pathways, analogous to those previously reported for the parent ion of piperazine, for example via internal α-cleavage.[38, 39] The base peak in the EI mass spectrum of 2,3-dioximino-piperazine is at m/z 43, and this is most probably due to the ion $[H_2NC{=}NH]^{+}$.

The isobutane PICI mass spectrum of 2,3-dioximino-piperazine (Table 3.14) shows a very prominent peak due to the ion $[M + H]^{+}$, which is in line with observations made for other dioximes. Fragment ions corresponding to losses of O and H_2O are also very prominent. Unlike the behaviour of this compound under EI conditions, the process of deoximation appears to be insignificant for this compound

under PICI conditions, as indicated by a peak of a very weak intensity at m/z 82. However, peaks of moderate intensity representing subsequent losses corresponding to those of piperazine are also observed in the isobutane PICI mass spectrum of this compound. Fragments at m/z values lower than 60 are not assigned, because many of these can arise from fragmentation of the isobutane itself.

Table 3.13 Ion Abundances in the EI Mass Spectrum of 2,3-Dioximino-piperazine

m/z	Intensity (%)	Assignment
144	9	$[M]^{+\cdot}$
128	28	$[M - O]^{+\cdot}$
127	8	$[M - OH]^{+}$
126	61	$[M - H_2O]^{+\cdot}$
114	14	$[M - NO]^{+}$
113	20	$[M - NOH]^{+\cdot}$
110	47	$[M - 2OH]^{+\cdot}$
112	45	$[M - 2O]^{+\cdot}$
96	17	$[M - H_2O - NO]^{+}$
86	16	$[HN(CH_2CH_2)_2NH]^{+\cdot}$
82	12	$[M - 2NOH]^{+\cdot}$
56	97	$[CH_2CH_2CHNH]^{+}$
55	61	$[CH_2CHNHCH]^{+\cdot}$
43	100	$[H_2NC{=}NH]^{+}$

Table 3.14 Ion Abundances in the Isobutane PICI Mass Spectrum of 2,3-Dioximino-piperazine

m/z	Intensity (%)	Assignment
145	97	$[M + H]^+$
144	11	$[M]^{+\cdot}$
129	98	$[(M + H) - O]^+$
127	39	$[(M + H) - H_2O]^+$
113	31	$[M - NOH]^{+\cdot}$
111	19	$[(M + H) - 2OH]^+$
82	1	$[M - 2NOH]^{+\cdot}$

3.3 General Assessment of the Mass Spectra of Dioximes

Generally, the principal fragmentation modes of the parent ion in the dioximes investigated under positive ion conditions include loss of HR, 2OH•, and loss of H_2O, leading to fragments such as $[CNO]^+$, $[R'CNO]^{+\cdot}$, $[RCN]^{+\cdot}$, and $[R'CN]^{+\cdot}$. The formation of the radical ion $[RCNO]^{+\cdot}$ probably occurs through a cycloreversion reaction. Such a reaction was previously suggested to occur during the formation of the ions $[HCNO]^{+\cdot}$, and $[PhCNO]^{+\cdot}$ from their corresponding furazan N-oxide or furazan ions.[40]

Dioximes with labile substituents, such as chlorine or tetrazole, show fragmentation pathways via rupture of the R-C bond, leading to ions such as furaxan, in which the labile substituent is absent. This contrasts the fragmentation pattern of aminoglyoxime and diaminoglyoxime in which the C-NH_2 bond remains intact during fragmentation. Deoximation, a process involved in the fragmentation of most dioximes with alkyl or aryl substituents, is not a common feature of the dioximes examined in the present study. On the other hand, C-C cleavage occurs in all dioximes except 1-amino-2-(benzyl-N-imino)glyoxime, and not unexpectedly, the cyclic 2,3-dioximino-piperazine.

With isobutane, all investigated dioximes form $[M + H]^+$ under positive ion chemical ionisation conditions, except those with the trinitroaromatic substituents. The preferrential

formation of $[M + H]^+$ ions rather than $[M + isobutane]^+$ adducts, is an indication of the pronounced proton affinity of these dioximes. Previous reports suggest that the site of protonation of oximic compounds may be the oxime group, although several possibilities of protonation site exist for these dioximes due to the complexity of their substituents. Loss of H_2O from the $[M + H]^+$ ion is common to all the isobutane PICI mass spectra.

A common feature among the negative ion chemical ionisation mass spectra of most of the investigated dioximes is a peak due to the anion $[M - H]^-$. In these spectra, peaks due to the $[M]^-$ anion are either absent or of very low intensity. This behaviour is in contrast to that involving aromatic compounds with nitro and nitroso groups in which non-dissociative electron capture occurs leading to highly abundant $[M]^-$ anions.[41] Processes involving dissociative electron capture and leading to the anions $[M - OH]^-$, $[M - H_2O]^{-\cdot}$, $[CNO]^-$, and $[CN]^-$ are also common in all the investigated vic-dioximes.

The behaviour of the dioximes studied under EI, PICI, and NICI mass spectrometric conditions reflect their thermal stability (Chapter 4). For example, the decomposition temperature of 1,2-di(3-nitrophenyl-N-amino)glyoxime (9), which gives a parent ion peak of moderate intensity in its EI spectrum, is higher than the other dioximes with polynitroaromatic substituents, the parent ion peaks of which are either absent or of weak intensity on their EI spectra.

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CHAPTER 4

4 Thermochemistry of Dioximes and of Their Copper(II) and Nickel(II) Complexes

4.1 Introduction

Studies on the thermal behaviour of dioximes and of their complexes have so far been limited.[1,2] The prime aim of the present investigation was to study the thermal properties and thermal decomposition of some dioximes and their copper(II) and nickel(II) complexes. An objective of this study was to correlate the results to the structures of these compounds.

During the last few years, a good deal of progress has been made in the study of the thermal decomposition of solids, particularly explosive materials.[3-6] Many thermal analytical techniques are available for the study of explosives, propellants and other systems, and these include differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC), dilatometry, and evolved gas analysis (EGA). However, most quantitative studies involve differential scanning calorimetry, in which the enthalpy change of a reaction is recorded as a function of temperature.

In the present investigation, the thermal decomposition of the dioximes and their complexes was mainly studied by differential scanning calorimetry. Thermogravimetry- a technique based on the mass change of a substance as a

function of temperature- was also applied, mainly to determine processes which involve mass changes such as dehydration.

Differential Scanning Calorimetry

A schematic representation of the differential scanning calorimetry system is shown in Figure 4.1. The temperature of the sample under investigation and the reference is increased using separate heating circuits. As the temperature of the sample is increased, any endothermic or exothermic changes taking place in the sample cause an adjustment of the heating rate to the system, in order to maintain both the sample and the reference at the same temperature. The quantity of this differential heating rate is measured against temperature to give a DSC curve. Typical DSC curves, obtained during this study, are shown in Figures 4.2 and 4.3. A downward peak arises by an exothermic reaction, whereas an upward peak arises by an endothermic reaction. The area under a peak of a DSC curve is directly proportional to the heat evolved or absorbed by the decomposing sample, and the height of the peak is directly proportional to the rate of the reaction. The area under the peak of a DSC curve divided by the weight of the sample gives the value of the heat of reaction.

The applications of differential scanning calorimetry have been extensive, and mainly involve the measurement of various physical constants.[7] Studies of decomposition kinetics, heats

of reaction, and estimation of activation energies of a wide range of compounds, particularly explosives, have been made in the past using differential scanning calorimeter.[8, 9] Such properties of the explosives have been used to obtain a better understanding of their thermal behaviour. For example, the heat of reaction obtained from DSC curves can be used to measure the critical temperature of explosion of pellets, and the useful life of an explosive which is terminated when 30% of an explosive has decomposed.[8]

The activation energy (Ea) constant is characteristic of the decomposition of a solid, and determines the influence of temperature on the decomposition rate. Generally, explosives decomposing exothermically with a high heat of reaction have high activation energy values.[9]

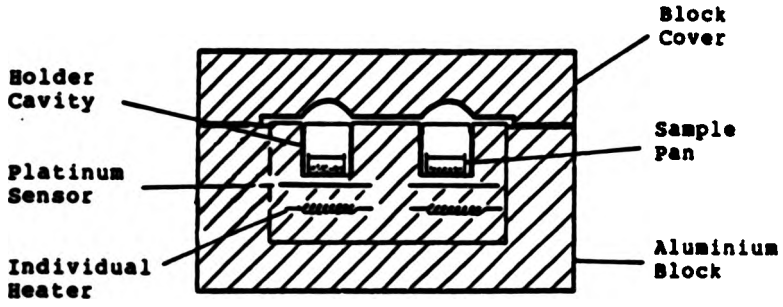


Figure 4.1 Schematic Diagram of a Differential Scanning Calorimeter System

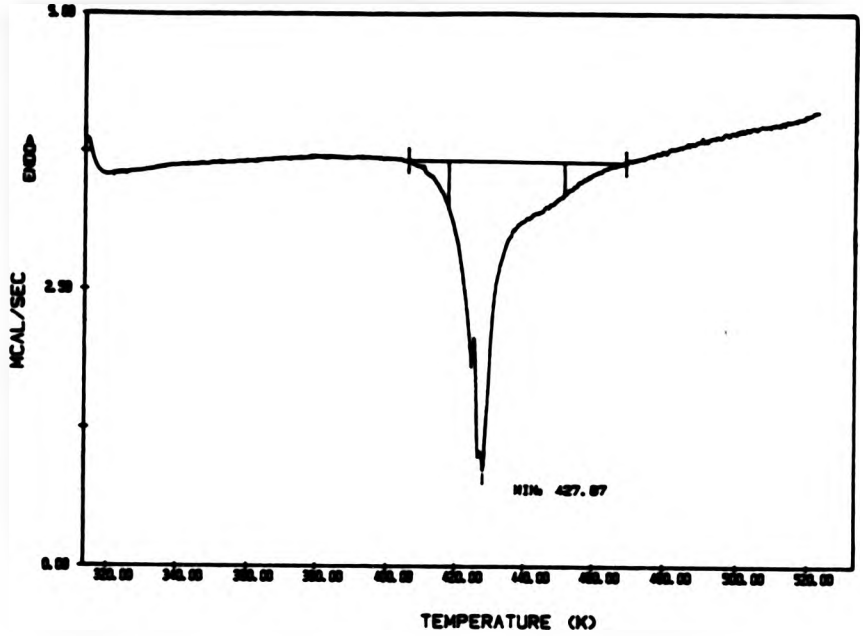


Figure 4.2 DSC Curve of 1,2-Di(5-tetrazolato)glyoxime

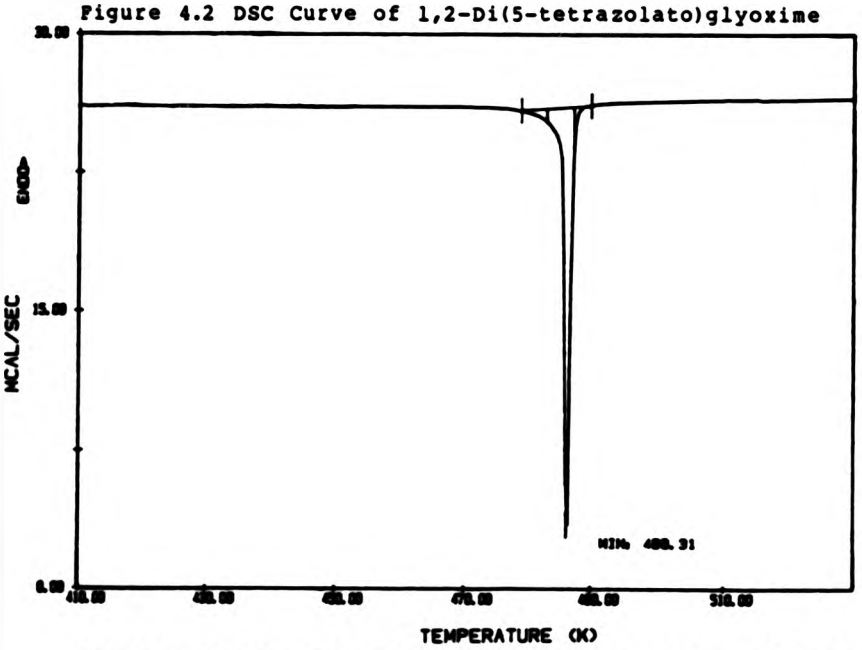


Figure 4.3 DSC Curve of Bis(1-amino-2-benzyl-N-imino-glyoximato)copper(II)

Thermogravimetry

In thermogravimetry, the mass of a sample is measured as its temperature is increased. A typical thermogravimetric instrument consists of an accurate balance, a heating device, and a temperature measurement and control device. The measured temperature is plotted against the change in the mass of the sample to give a TG curve. Figure 4.4 shows a typical TG curve obtained in the course of the present study.

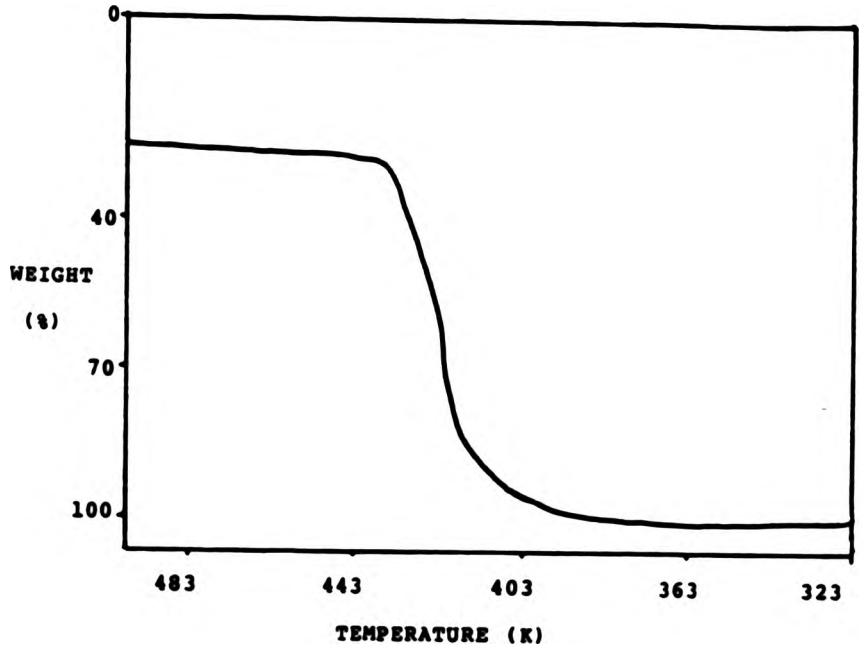
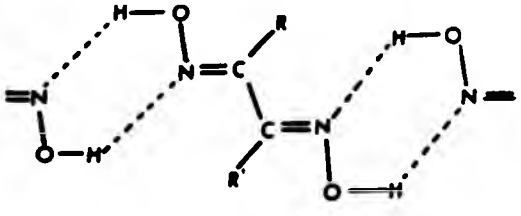


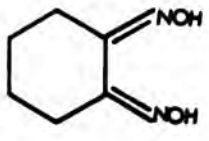
Figure 4.4 TG Curve of 1,2-Di(5-tetrazolato)glyoxime

4.2 Thermal Decomposition of Dioximes

The dioximes studied by differential scanning calorimetry, and their decomposition temperatures are listed in Table 4.1. All dioximes decompose exothermically at high temperatures, and complete decomposition occurs up to 530 K. The high decomposition temperature of these dioximes may be related with the extensive intermolecular hydrogen bonding present. Previously, the high melting point of dimethylglyoxime (513 - 514 K), has been correlated with its structure,[10] which involves planar, centro-symmetric molecules linked together by hydrogen bonds O-H---N (4.1; R= Me).[11] In alicyclic dioximes having the cis configuration, such as cyclohexaneglyoxime (4.2), free rotation around the bond involving the oximino carbons is prevented by the ring. Generally, the decomposition temperatures of alicyclic dioximes such as cyclohexaneglyoxime (458 - 461 K) are lower than aliphatic dioximes.



4.1



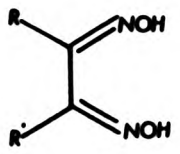
4.2

Table 4.1 Differential Scanning Calorimetric Results of Some Dioximes (4.3)

Compound Number	Dioxime R	Dioxime R'	Mass (mg)	Temperature at which peak starts (K)	Temperature at which peak is at maxima (K)	Temperature at which peak ends (K)
1	H	Cl	1.31	353	377	385
				385	413	446
2	Cl	Cl	1.13	480	481	509
3	H	NH_2	1.22	406	423	445
4	NH_2	NH_2	1.30	450	474	492
5	H	tH	0.98	407	424	441
6	tH	tH	1.73	406	428	470
7	H	tCl	1.24	434	464	482
8	tCl	tCl	0.78	426	440	462
9	C_6H_5NH	C_6H_5NH	1.11	478	491	501

Table 4.1 (continued)

Compound Number	Dioxime R	Dioxime R'	Mass (mg)	Temperature at which peak starts (K)	Temperature at which peak is at maxima (K)	Temperature at which peak ends (K)
10	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	1.14	381	425	453
				459	484	510
11	NH_2	$C_6H_3(NO_2)_2NH$	1.19	411	448	470
12	NH_2	$C_6H_2(NO_2)_3NH$	1.26	409	422	443
13	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	0.85	392	398	409
				508	524	533
14	NH_2	$C_6H_5C(H)N$	1.29	453	464	471
				471	483	501

4.3= 

Generally, the DSC curves of the dioximes investigated show one exothermic peak in the range 420 - 530 K. The DSC curve of anti-chloroglyoxime (1)* contains two exothermic peaks at 377 and 413 K (Figure 4.5). This is in agreement with the TG curve of the compound, which shows a loss of 30% due to loss of HCl in the range of 357 - 363 K (theoretical value based on the loss of one HCl molecule is 30%). This is followed by decomposition at 413 K (Figure 4.6). Loss of HCl from anti-chloroglyoxime leads to the formation of the nitrile oxide 4.4 (Scheme 4.1). Formation of this nitrile oxide was previously described in a study involving the structure and chemical reactivity of the compound.[12] Decomposition of anti-chloroglyoxime via the loss of hydrogen chloride is supported by the mass spectrum of the dioxime, which shows a peak of high intensity corresponding to loss of HCl from the parent ion peak (Chapter 3).

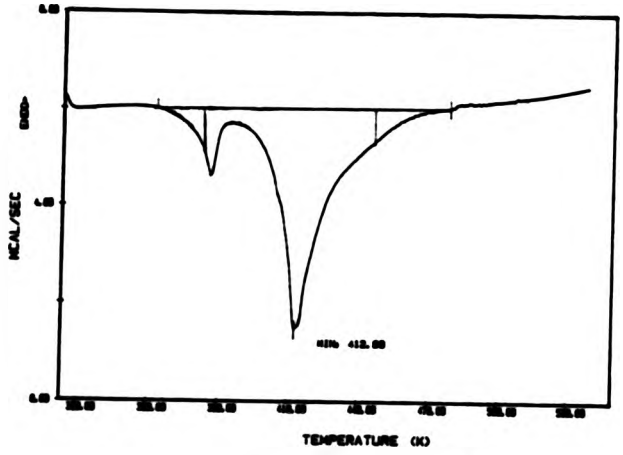


Figure 4.5 DSC Curve of anti-Chloroglyoxime

*number refers to compound number in Table 4.1

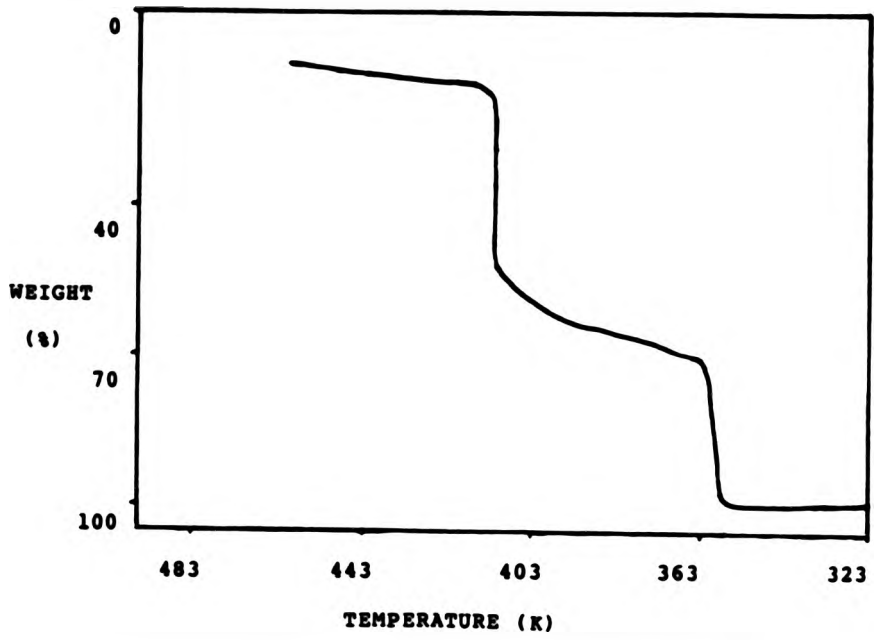
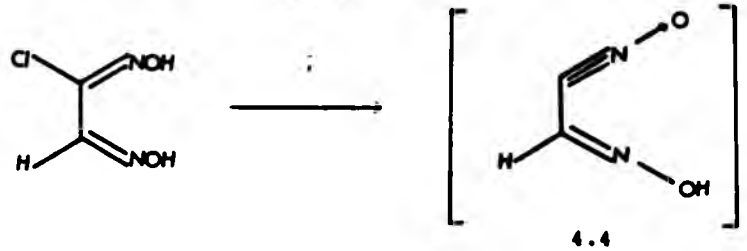


Figure 4.6 TG Curve of anti-Chloroglyoxime



4.4

Scheme 4.1

The DSC curve of 1-amino-2-(benzyl-N-imino)glyoxime (14) shows two exothermic peaks at 464 and 483 K. An inspection of the TG curve of this dioxime shows no weight loss up to 470 K, but decomposition occurring at 475 - 490 K. This suggests that the first peak in the DSC curve of this compound (464 K) may be due to its melting, and the second

peak (483 K) due to its decomposition. Similarly, the DSC curve of 1,2-di(3-nitrophenyl-N-amino)glyoxime (10) shows two peaks at 425 and 484 K, the former arising from the melting of the solid, and the latter being due to its decomposition.

Among the dioximes with nitroaromatic substituents (10 - 13), an increase in the number of nitro groups cause destabilisation as indicated by a lowering of the decomposition temperatures in the sequence:

Compound 10> Compound 11> Compound 12> Compound 13

Thus, the initial decomposition temperatures of the symmetric dioximes 1,2-di(phenyl-N-amino)glyoxime (9), 1,2-di(3-nitrophenyl-N-amino)glyoxime (10), and 1,2-di(2,4,6-trinitrophenyl-N-amino)glyoxime (13) are 491, and 425, and 398 K, respectively. The destabilisation of these dioximes due to the increasing number of nitro groups is in line with the mass spectral observations (Chapter 3). These show that the EI mass spectrum of 1,2-di(3-nitrophenyl-N-amino)-glyoxime (10) gives a parent ion peak of moderate intensity, that of 1-amino-2-(2,4-dinitrophenyl-N-amino)glyoxime (11) gives a parent ion peak of weak intensity, whereas those of 1-amino-2-(2,4,6-trintrophenyl-N-amino)glyoxime (12) and 1,2-di(2,4,6-trinitrophenyl-N-amino)glyoxime (13) give no parent ion peaks.

An interesting conclusion which has arisen from the present study is that symmetric dioximes (R = R') decompose at temperatures relatively higher than their respective

asymmetric dioximes ($R \neq R'$). For example, the symmetric diaminoglyoxime (4) decomposes at 474 K, whereas asymmetric aminoglyoxime (3) decomposes at 423 K. Similarly, 1,2-di-(2,4,6-trinitrophenyl-N-amino)glyoxime (13) decomposes at 524 K, whereas 1-amino-2-(2,4,6-trinitrophenyl-N-amino)-glyoxime (12) decomposes at 422 K. Although not previously considered, this trend is also evident from literature data on the decomposition temperatures of other dioximes with alkyl or aryl substituents. Thus, the decomposition temperature of the asymmetric methylglyoxime (429 K)[12, 13] is lower than that of the symmetric dimethylglyoxime (513 - 514 K).[10] Also, the decomposition temperature of phenylglyoxime (446 K)[14] is lower than that of anti-diphenylglyoxime (479 - 480 K).[15]

The decomposition temperatures of dioximes with tetrazolyl substituents (5-8) are generally lower than those of the other dioximes investigated in this study. These compounds may decompose via complex decomposition pathways. The difference in the decomposition temperature of symmetric and asymmetric dioximes (i.e., the higher stability of the former), is also evident from this group of dioximes. In addition, it can be seen that the decomposition temperatures of the dioximes with the tCl substituents (7, 8) are higher than those with the tH substituents (5, 6). This may reflect the participation of Cl in intra- or intermolecular bonding involving O-H-Cl bridges in the dioximes with the tCl substituents.

4.3 Heat of Reaction and Activation Energy of Dioximes

The heat of reaction during the decomposition of various dioximes was also determined from their DSC curves (Table 4.2). As discussed earlier, this is obtained from the area of the DSC trace divided by the weight of the investigated sample. In addition, DSC was also used to determine the activation energies of these dioximes (Table 4.2).

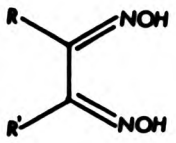
In this study, the values of the heat of reaction usually refer to the final decomposition temperature. In the case of anti-chloroglyoxime (1), the measured amount of the heat of reaction involves both successive stages of the decomposition reactions, corresponding to the peaks at 377, and 413 K. Among the dioximes investigated, anti-chloroglyoxime decomposes with the maximum evolution of heat (-2385 J/g). In contrast, the amount of heat evolved in the decomposition of dichloroglyoxime is comparatively smaller (-280 J/g).

The activation energy involved in the decomposition reaction of 1-amino-(2-benzyl-N-imino)glyoxime (14) is surprisingly high, and in fact, is the highest among the dioximes investigated in this work (1093.0 KJ/mol). As discussed before (Section 4.1), solids which decompose with a high heat of reaction show high activation energies. However, the heat of reaction involved in the decomposition of 1-amino-2-(benzyl-N-imino)glyoxime is relatively low (-228 J/g).

Table 4.2 Thermal Kinetic Parameters of Some Dioximes (4.3)

Compound Number	Dioxime R	Dioxime R'	Amount of Heat Evolved, ΔH (J/g)	Activation Energy, Ea (KJ/mol)
1	H	Cl	-2385	81
2	Cl	Cl	-280	20
4	NH_2	NH_2	-782	675
6	tH	tH	-514	443
7	H	tCl	-551	365
12	NH_2	$C_6H_3(NO_2)_3NH$	-429	366
13	$C_6H_3(NO_2)_3NH$	$C_6H_3(NO_2)_3NH$	-871	973
14	NH_2	$C_6H_5C(H)N$	-228	1093

4.3-



4.4 Thermal Decomposition of Copper(II) and Nickel(II) Complexes of Dioximes

The decomposition temperatures of the copper(II) and nickel(II) complexes involving two glyoximato monoanions per metal ($M(LH)_2$; LH_2= dioxime) are presented in Table 4.3. The decomposition temperature of the copper(II) and nickel(II) complexes of the tetrazolyl-substituted dioximes which involve the dianion of the dioxime per metal in a 1:1 ratio ($M(L).2H_2O$; LH_2= dioxime) are listed in Table 4.4.

Complexes of type $M(LH)_2$

Like the free dioximes, all copper(II) and nickel(II) complexes of type $M(LH)_2$ investigated show highly exothermic decompositions. The TG curves of these complexes show no weight loss prior to decomposition. In the case of bis-(diaminoglyoximato)copper(II) monohydrate (16)*, its TG curve (Figure 4.7) shows a loss of 5% due to loss of one water molecule at 392 - 398 K per one molecule of the complex (theoretical value based on the loss of one water molecule is 6%). This corresponds to an endothermic peak on its DSC curve appearing at 399.5 K (Figure 4.8), which was obtained under the same conditions as that for the TG curve (heating rate of 10 ^{o}C/min, and in an atmosphere of nitrogen).

*number refers to compound number in Table 4.3

Table 4.3 Differential Scanning Calorimetric Results of the Nickel(II) and Copper(II) Complexes of Type 4.5

Compound Number	Dioxime R	Dioxime R'	Metal (M)	Mass (mg)	Temperature at which peak starts (K)	Temperature at which peak is at maxima (K)	Temperature at which peak ends (K)
15	NH_2	NH_2	Ni	1.54	541	577	597
16	NH_2	NH_2	Cu	1.41	370	399	412
					463	486	487
17	C_6H_5NH	C_6H_5NH	Ni	1.36	527	534	540
18	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Ni	1.73	527	566	589
19	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Cu	1.00	531	542	569
20	NH_2	$C_6H_3(NO_2)_2NH$	Ni	0.52	502	534	562
21	NH_2	$C_6H_3(NO_2)_2NH$	Cu	1.14	448	490	511
22	NH_2	$C_6H_2(NO_2)_3NH$	Ni	0.84	431	498	562

Table 4.3 (continued)

Compound Number	Dioxime R	Dioxime R'	Metal (M)	Mass (mg)	Temperature at which peak starts (K)	Temperature at which peak is at maxima (K)	Temperature at which peak ends (K)
23	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	Ni	0.95	506	539	562
24	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	Cu	1.11	500	529	554
25	NH_2	$C_6H_5C(H)N$	Ni	1.54	467	474	484
26	NH_2	$C_6H_5C(H)N$	Cu	1.17	479	486	490

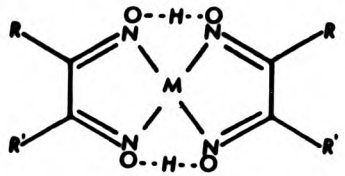
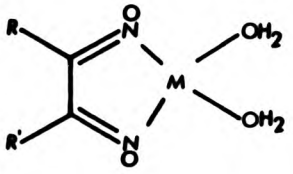
4.5= 

Table 4.4 Differential Scanning Calorimetric Results of the Nickel(II) and Copper(II) Complexes of the Type 4.6

Compound Number	Dioxime R	Dioxime R'	Metal (M)	Mass (mg)	Temperature at which peak starts (K)	Temperature at which peak is at maxima (K)	Temperature at which peak ends (K)
27	H	tH	Cu	0.77	351	370	381
28	H	tCl	Cu	1.36	363	420	473
29	tH	tH	Ni	4.02	426	447	479
30	tH	tH	Cu	4.32	366	390	392
					392	395	397
31	tCl	tCl	Ni	1.31	410	423	428
32	tCl	tCl	Cu	1.87	397	404	420

4.6=



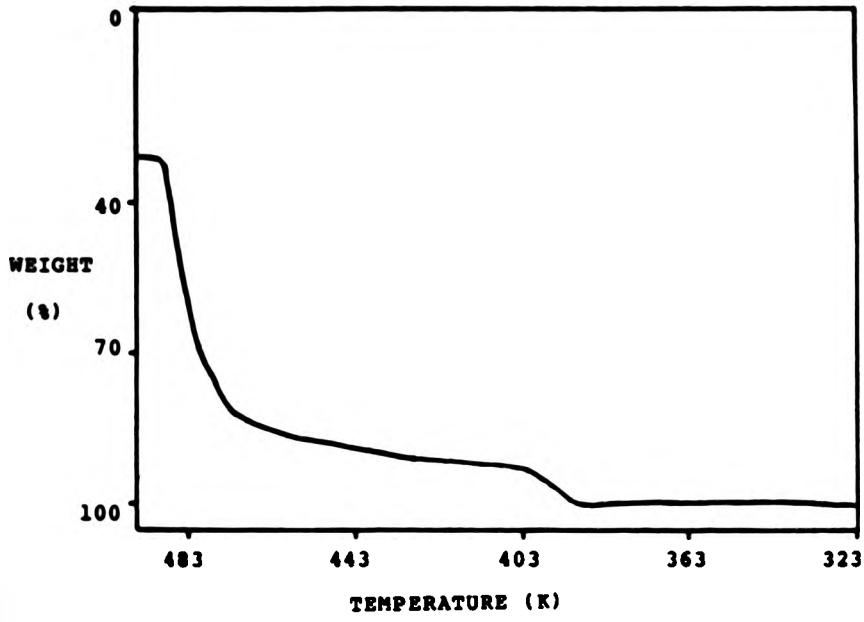


Figure 4.7 TG Curve of $Cu(dagH)_2.H_2O$

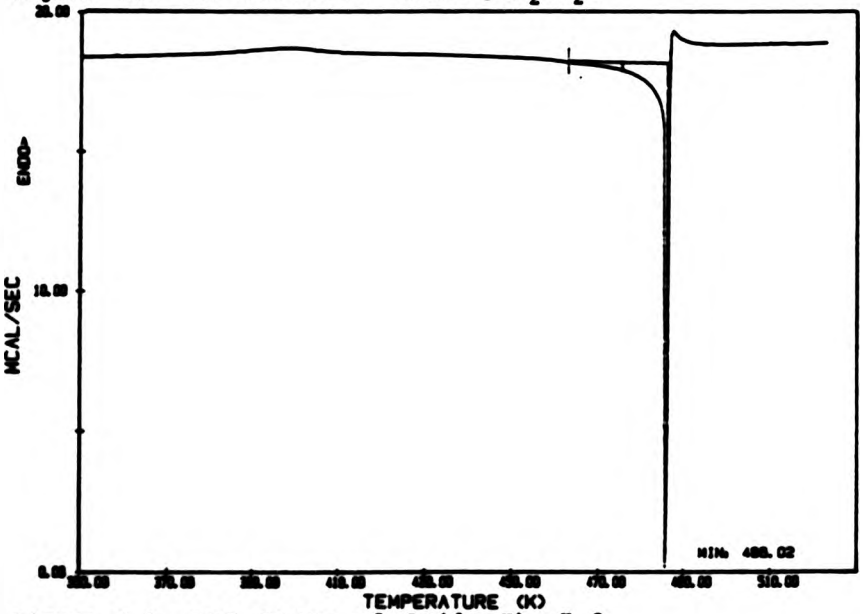


Figure 4.8 DSC Curve of $Cu(dagH)_2.H_2O$

The nickel(II) and copper(II) complexes which involve two monoanions of a dioxime per metal (Table 4.3) decompose at temperatures relatively higher than those for their corresponding free ligands. For example, the nickel(II) complex of 1,2-di(3-nitrophenyl-N-amino)glyoxime (18) decomposes at 566 K, and the copper(II) complex of the same dioxime (19) decomposes at 542 K, whereas the free dioxime (10) decomposes at 484 K. This suggests that the nickel(II) and copper(II) complexes of a particular dioxime have greater thermal stability than their free ligands. There are many factors which influence the thermal stability of the complexes of dioximes. These include the formation of hydrogen bridges between the two chelated ligands in the complex, and π-bonding between the metal and the ligand.[16]

The decomposition temperatures of the nickel(II) and copper(II) complexes vary with the type of substituent on the dioxime. Certain trends observed in the decomposition temperatures of the free dioximes are also observed for these complexes:

(i) The nickel(II) and copper(II) complexes of the asymmetric dioximes listed in Table 4.3 decompose at temperatures lower than those for the complexes of symmetric dioximes.

(ii) In the case of dioximes with polynitroaromatic substituents, an increase in the number of nitro groups lowers the decomposition temperature of the corresponding nickel(II) and copper(II) complexes. Thus, bis(1,2-di(3-nitrophenyl-N-amino)glyoximato)nickel(II) (18) decomposes at

566 K, whereas bis(1,2-di(2,4,6-trinitrophenyl-N-amino)-glyoximato)nickel(II) (23) decomposes at 539 K. A similar observation can be made among the copper(II) complexes of these dioximes. Thus, bis(1,2-di(3-nitrophenyl-N-amino)-glyoximato)copper(II) (19) decomposes at 542 K, whereas bis(1,2-di(2,4,6-trinitrophenyl-N-amino)glyoximato)copper(II) (24) decomposes at 529 K.

Another observation of the present study is that nickel(II) complexes with a square planar structure decompose at temperatures higher than those with a non-planar structure. Thus, the square planar nickel(II) complexes of diaminoglyoxime (15), 1,2-di(3-nitrophenyl-N-amino)glyoxime (18), and 1,2-di(phenyl-N-amino)glyoxime (17) decompose at 577, 566, and 534 K, respectively. On the other hand, the non-planar nickel(II) complexes of 1-amino-2-(benzyl-N-imino)glyoxime (25), 1-amino-2-(2,4,6,-trinitrophenyl-N-amino)glyoxime (22), 1-amino-2-(2,4-dinitrophenyl-N-amino)-glyoxime (20), and 1,2-di(2,4,6-trinitrophenyl-N-amino)-glyoxime (23) decompose at 474, 498, 534, and 539 K, respectively.

Among the planar nickel(II) complexes (15, 17, and 18), a correlation between their decomposition temperatures and shifts of the ν(C=N) band on their i.r. spectra is evident (Table 4.5). The shift of the ν(C=N) band of these complexes compared to the free ligands depends on the length of the nickel-ligand bond which indicates its strength. Thus, among the concerned complexes, the greatest shift of the

ν(C=N) band occurs for the nickel(II) complex of diaminoglyoxime (15), which has the highest decomposition temperature (Table 4.5).

Table 4.5 Correlation of the Decomposition Temperature of Some Nickel(II) Dioximato Complexes with Shifts of Their ν(C=N) i.r. Bands

R	R'	ν(C=N) of Free Dioxime (cm^{-1})	ν(C=N) of Ni(II) Complex (cm^{-1})	Decomposition Temperature (K)
NH_2	NH_2	1640	1590	577
$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	1610	1575	566
C_6H_5NH	C_6H_5NH	1640	1605	534

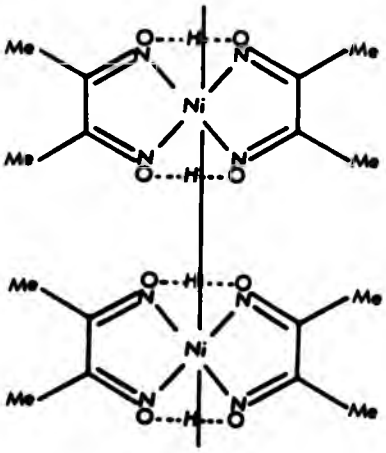
With the complexes involving two monoanionic glyoximato liganda (Table 4.3), the copper(II) complexes decompose at lower temperatures than their corresponding nickel(II) complexes. For example, the copper(II) complex of 1,2-di(3-nitropheny-N-amino)glyoxime (19) decomposes at 542 K, whereas the corresponding nickel(II) complex (18) decomposes at 566 K. This difference in decomposition temperature between copper(II) and nickel(II) glyoximato complexes may be correlated with oxidation state characteristics, and structural factors.

In the case of the copper(II) complexes, decomposition may take place with the reduction of Cu(II) to Cu(I), a process not possible in the case of the nickel(II) complexes. The reduction of Cu(II) to Cu(I) has been described to occur during the decomposition of other copper(II) complexes, such as that of (dimethylglyoxime)copper(II) chloride,[17] and the tetrammine cupric sulphate.[18]

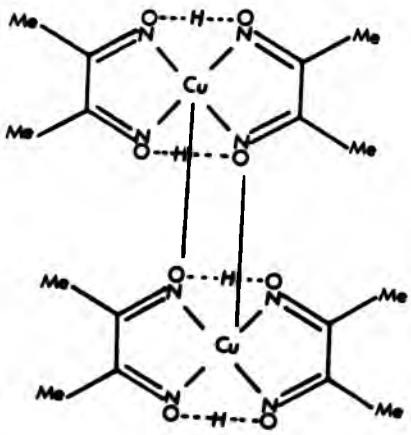
The structures of bis(dimethylglyoximato)nickel(II),[19] and bis(dimethylglyoximato)copper(II)[20] have been determined by X-ray crystallographic studies. Both structures show intermolecular hydrogen bonding between the hydroxyl groups of opposite glyoximato units. Although the structure of the $M(LH)_2$ unit in the copper(II) and nickel(II) complexes of dimethylglyoxime is almost identical, they have important differences which may affect their thermal behaviour. In the nickel(II) complex, weak intermolecular nickel-nickel bonds exist, with the nickel atoms of the square planar structures stacked one above another (4.7), resulting in a polymeric structure. Instead, no copper-copper bonds exist in the copper(II) complex, but long copper-oxygen bonds join two neighbouring complex molecules, resulting in a dimeric structure (4.8).[21]

By analogy with the copper(II) and nickel(II) complexes of dimethylglyoxime, it may be suggested that metal-metal bonds exist in the square planar nickel(II) complexes investigated in this study (listed in Table 4.3), but no such bonds exist for the respective copper(II) complexes. Thus, it appears

that the higher decomposition temperatures of the investigated planar nickel(II) complexes compared to those of the copper(II) complexes, are because of the increased stability of the nickel(II) complexes arising from the nickel-nickel bonding. In the case of the nickel(II) complexes, an increase in the bulkiness of the dioxime group leads to a lowering of the decomposition temperature, probably because of weakening of the Ni-Ni bond. Thus, the nickel(II) complex of diaminoglyoxime (15) decomposes at 577 K, whereas the nickel(II) complex of 1,2-di(phenyl-N-amino)glyoxime (17) decomposes at the lower temperature of 534 K. Previously, it has been found that an increase in the bulkiness of the dioxime group in nickel(II) complexes, leads to longer, and hence weaker nickel-nickel bonds.[22] For example, the nickel-nickel bond in the nickel(II) complex of 1,2-cyclohexaneglyoxime (3.24 Å) is shorter than that in 3-methyl-1,2-cyclohexaneglyoxime (3.47 Å).



4.7



4.8

Complexes of type $M(L).2H_2O$

Like the complexes of type $M(LH)_2$, the copper(II) complexes of type $M(L).2H_2O$ decompose at temperatures lower than the corresponding nickel(II) complexes. On the other hand, unlike the complexes of type $M(LH)_2$, the complexes of type $M(L).2H_2O$ generally decompose at temperatures lower than their corresponding ligands.

For the hydrated complexes $M(L).2H_2O$, which involve the dianions of the tetrazolyl-substituted dioximes (27-32)*, loss of water and decomposition occur simultaneously as indicated by their DSC and TG curves. Even at lower heating rates, no endothermic peaks due to the dehydration of these products were obtained on their DSC curves. For example, the DSC curve of mono(1,2-di(5-tetrazolato)glyoximato)copper(II) dihydrate (30) shows an exothermic peak at 395 K (Figure 4.9). Furthermore, the corresponding TG curves of the complexes involving the tetrazolyl-substituted dioximes confirm that the water alone could not be removed from these complexes. Thus, the TG curve of mono(1,2-di(5-tetrazolato)-glyoximato)copper(II) dihydrate (30) shows a loss of 81% at 392 - 398 K (Figure 4.10). This weight loss is due to extensive decomposition of the complex, and not due to the dehydration of the complex which should theoretically correspond to a weight loss of 9%.

*number refers to compound number in Table 4.4

The nickel(II) and copper(II) complexes of the tetrazolyl-substituted dioximes (Table 4.4) show initial exothermic decompositions which occur at relatively lower temperatures than the other complexes discussed so far. This is probably related to the structure of these complexes in which only one dianionic ligand is present (4.6), and no hydrogen bridges of the type found in the complexes containing two monoanionic ligands exist (4.5). Also, the nature of the dioxime substituent influences the thermal decomposition of these complexes. Like the corresponding free ligands, the introduction of chlorine in the tetrazolyl ring increases the stability of the complexes. For example, the copper(II) complex of 1-(5-chlorotetrazolyl)glyoxime (28) decomposes at 420 K, whereas that of 1-(5-tetrazolyl)glyoxime (27) decomposes at 370 K.

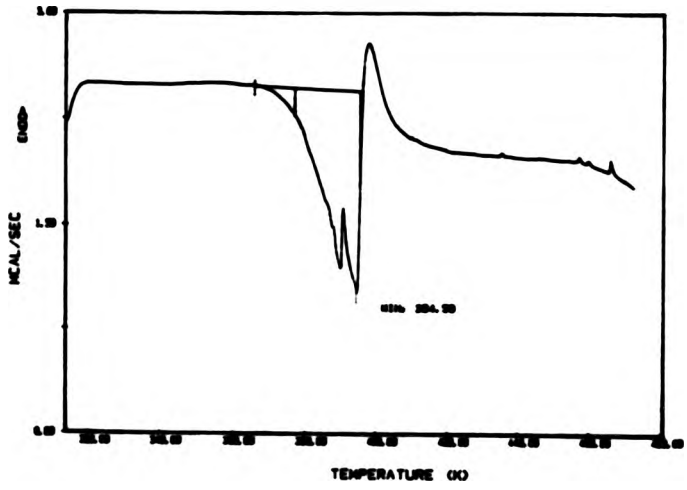


Figure 4.9 DSC Curve of Mono(1,2-di(5-tetrazolato-glyoximato)copper(II) Dihydrate

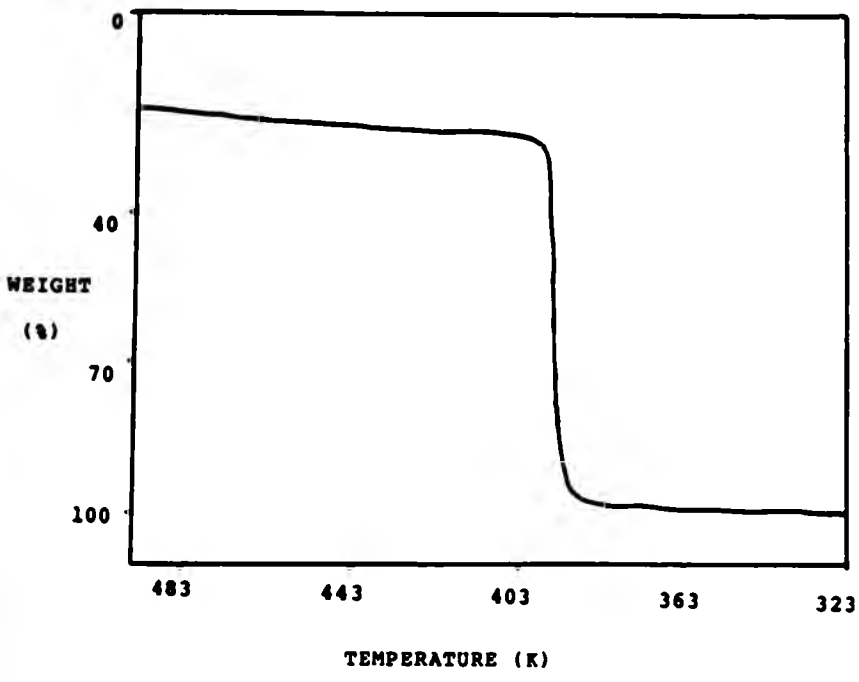


Figure 4.10 TG Curve of Mono(1,2-di(5-tetrazolato-glyoximato)copper(II) Dihydrate

4.5 Heat of Reaction and Activation Energy of Copper(II) and Nickel(II) Glyoximato Complexes

The heat of reaction and the activation energy involved in the decomposition of selected glyoximato complexes of type $M(LH)_2$ studied in the present work are listed in Table 4.6. In addition, the heat evolved and activation energy were determined for two complexes of tetrazolyl-substituted dioximes of the type $M(L).2H_2O$, and these were found to be lower than those of the complexes of type $M(LH)_2$. The heat evolved in the decomposition of the copper(II) complexes of 1-(5-chlorotetrazolato)glyoxime (28) and 1,2-di(5-tetrazolato)glyoxime (30) were found to be -558 and -92 J/g, respectively. The activation energy of the former was found to be 172 KJ/mol, and that of the latter 173 KJ/mol.

In the case of the copper(II) and nickel(II) complexes of the type $M(LH)_2$, the values of the heat evolved for their decomposition are generally higher than those involved for their respective ligands. With the exception of 1-amino-2-(benzyl-N-imino)glyoxime (14), and its copper(II) and nickel(II) complexes (26 and 25, respectively), the activation energies of the complexes are lower than their corresponding ligands. Like in the case of the respective free dioxime, the activation energies involved in the decomposition of the copper(II) and nickel(II) complexes of 1-amino-2-(benzyl-N-imino)glyoxime, are unexpectedly high (2275 and 2065 KJ/mol, respectively).

A comparison between the thermal kinetic parameters of the copper(II) and nickel(II) complexes (Table 4.6), indicates that during decomposition, the heat of reaction and the activation energy of the copper(II) complex of a particular ligand are higher than those for the corresponding nickel(II) complex. This suggests that the copper(II) complexes are generally more energetic in nature than the corresponding nickel(II) complexes. Qualitative tests examining the impact sensitivity of these compounds under the conditions generally used for testing primary explosives, indicate that the copper(II) complexes of some dioximes are sensitive upon impact, whereas the corresponding nickel(II) complexes are not. For example, the copper(II) complex of 1,2-di(5-tetrazolato)glyoxime (30) detonates upon mechanical impact using very small quantities (> 4 mg), whereas the nickel(II) complex of the same ligand (29) remains intact upon mechanical impact, irrespective of sample quantity. This was confirmed by studying the i.r. spectra of the residual samples after the mechanical impact test.

Values for the heat evolved and activation energy in the decomposition of some of the complexes investigated in this study are comparable to those for compounds of explosive nature such as mercuric 5-nitrotetrazole (ΔH= -2138 J/g, Ea= 114 KJ/mol),[23, 24] β-lead azide (ΔH= -1280 J/g),[8] and lead azotetrazole (ΔH= -665 J/g, Ea= 167 KJ/mol).[8, 25]

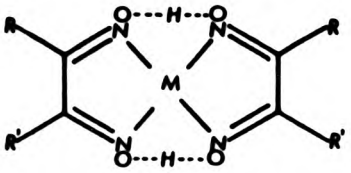
Table 4.6 Thermal Kinetic Parameters of Some Nickel(II) and Copper(II) Complexes of Dioximes of the Type 4.5

Compound Number	Dioxime R	Dioxime R'	Metal (M)	Amount of Heat Evolved ΔH, J/g	Activation Energy Ea KJ/mol
15	NH_2	NH_2	Ni	-177	199
16	NH_2	NH_2	Cu	-385	223
17	C_6H_5NH	C_6H_5NH	Ni	-434	1178
18	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Ni	-909	453
19	$C_6H_4(NO_2)NH$	$C_6H_4(NO_2)NH$	Cu	-1304	511
22	NH_2	$C_6H_2(NO_2)_3NH$	Ni	-1257	87

Table 4.6 (continued)

Compound Number	Dioxime R	Dioxime R'	Metal (M)	Amount of Heat Evolved ΔH, J/g	Activation Energy Ea KJ/mol
23	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	Ni	-1932	642
24	$C_6H_2(NO_2)_3NH$	$C_6H_2(NO_2)_3NH$	Cu	-2648	874
25	NH_2	$C_6H_5C(H)N$	Ni	-272	2065
26	NH_2	$C_6H_5C(H)N$	Cu	-617	2275

4.5=



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CHAPTER 5

5 Experimental

5.1 General

5.1.1 Reagents and Solvents

Most reagents were obtained commercially as reagent grade chemicals and were employed without further purification. Certain liquid reagents and solvents, such as dichloromethane and toluene, were purified by distillation immediately before use. Methanol, ethanol, and acetone were kept dry over molecular sieve, and diethyl ether over sodium.

Published methods were applied for the preparations of 1,2-ethanedionedioxime,[1] 1,2-diamino-1,2-ethanedionedioxime,[2] 1,2-dichloro-1,2-ethanedionedioxime,[3] and 1,2-di(phenyl-N-amino)-1,2-ethanedionedioxime.[4] The method of preparation of *amphi* 1-chloro-1,2-ethanedionedioxime was slightly modified to that reported in the literature,[5] and this is given in Section 5.2. *Anti* 1-chloro-1,2-ethanedionedioxime was prepared by passing hydrogen chloride gas through *amphi* 1-chloro-1,2-ethanedionedioxime in diethyl ether, as previously reported.[6] Methods already reported in the literature were also applied for the syntheses of the complexes bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II),[7] bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate,[8] bis(1,2-diphenyl-1,2-ethanedionedioximato)copper(II),[9] bis(1,2-diphenyl-1,2-ethanedionedioximato)nickel(II),[10] bis(1,2-

dimethyl-1,2-ethanedionedioximato)nickel(II),[10] and bis-(cyclohexane-1,2-ethanedionedioximato)nickel(II).[11] Ethylene-bisacetamide,[12] and disodium ethane-bis-nitraminate,[13] were also prepared according to published methods.

5.1.2 General Techniques

Certain reactions involving reactants and/or products of explosive nature were conducted in armoured cupboards at the Royal Armament Research and Development Establishment (RARDE). Relevant experiments are marked with an asterisk (*). Any precipitates were filtered by gravity in anti-static gutta-percha filter funnels. Such compounds were dried on a steam heated drying table operating at ca. 40 ^{o}C. Conducting polypropylene pots were used for the storage of these compounds.

Pre-coated silica gel 60 plates of 0.25 mm thickness, and dimensions of about 6 x 2 cm were used for thin layer chromatography. The silica gel adsorbent used in column chromatography techniques was Kieselgel 60 silica with a mesh size of 70 - 230.

5.1.3 Analytical Techniques

Cobalt, nickel, and copper were determined by the method of atomic absorption spectrometry. A known mass of the sample (ca. 0.1 g) under investigation was warmed with concentrated

nitric acid (ca. 2 cm^3) and concentrated sulphuric acid (ca. 1 cm^3). The sample was digested further with hydrogen peroxide (ca. 1 cm^3). Volumetric solutions of the digested sample were then analysed using a SP9 atomic absorption spectrometer.

For nickel, gravimetric analysis using 1,2-dimethyl-1,2-ethanedionedioxime was also applied after wet oxidation of the sample. Nickel was precipitated by the addition of an alcoholic solution of 1,2-dimethyl-1,2-ethanedionedioxime to a hot, faintly acidic solution of the nickel sample, and then adding a slight excess of aqueous ammonia solution. The precipitate was washed with cold water and then weighed as bis(1,2-dimethyl-1,2-ethanedionedioximato)nickel(II) after drying at 110 - 120 ^oC.

Carbon, hydrogen, and nitrogen were determined by the microanalytical services at RARDE and the Polytechnic of North London (PNL).

Chlorine was determined titrimetrically after combustion of the sample using the oxygen flask method.[14]

5.1.4 Physical Techniques

Infrared Spectroscopy

Infrared spectra were recorded in the region 600 - 4000 cm^{-1} on a Perkin Elmer 781 infrared spectrophotometer using KBr discs.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectra were recorded using a Bruker WP80 spectrophotometer. ^{1}H nuclear magnetic resonance spectra were recorded in the range 0 - 20 ppm with integration trace. Solutions for both ^{1}H and ^{13}C nuclear magnetic resonance studies were prepared with common organic deuterated solvents, using tetramethylsilane (TMS) as the standard reference. In the case of solutions in deuterated water, the standard reference used was the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid.

Ultraviolet and Visible Spectroscopy

Ultraviolet and visible spectra were recorded in the region 200 - 900 nm using a Perkin Elmer Lambda 5 spectrophotometer.

Mass Spectrometry

Mass spectra were obtained using a AEI/MSS MS9 at PNL or a VG Analytical 7070 EQ mass spectrometer at RARDE. Chemical ionisation mass spectra were obtained using methane or isobutane as reagent gases. Accurate mass measurements were done at 2000 - 3000 resolution.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TG) curves were obtained under nitrogen using a Perkin Elmer TGS 2 instrument. These were

normally obtained using scan rates of 10 $^{o}C\ min^{-1}$ on samples of 0.5 - 1.0 mg mass.

Differential Scanning Calorimetry

Differential scanning calorimetric (DSC) investigations were carried out on a Perkin-Elmer DSC2 instrument at RARDE. The DSC curves were normally obtained at a scanning rate of 10 $^{o}C\ min^{-1}$. The atmosphere was nitrogen at a flow rate of 10 $cm^{3}\ min^{-1}$. The samples were sealed in aluminium pans.

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were made using a J.M.C Johnson Matthey magnetic susceptibility balance. The apparatus was calibrated using mercury tetrathiocyanato-cobaltate(II). Diamagnetic corrections were made using Pascal's constants.[15]

Conductance Measurements

Conductance measurements were made using a PTI-18 digital conductivity meter.

X-ray Crystallogaphy

X-ray crystallographic data were obtained using a Phillips PW1100 four-circle diffractometer, with Mo $K\alpha$ radiation. Computations were performed with SHELX76.[16]

5.2 Reactions

1. Preparation of amphi 1-Chloro-1,2-ethanedionedioxime

Chloral hydrate (50.0 g, 300 mmol) was added to a solution of hydroxylammonium chloride (63.0 g, 900 mmol) and sodium hydroxide (48.0 g, 450 mmol) in water (300 cm^3) and the resulting mixture was allowed to stand at 0 °C (6 h). Sodium hydroxide (54%, 100 cm^3) was gradually added to the cold mixture, which was subsequently acidified with concentrated sulphuric acid (pH 6). Removal of the solvent from the mixture gave amphi 1-chloro-1,2-ethanedionedioxime hydrate (26.7 g, 72%) m.p., 116 - 118 °C (dec.) (lit., 100 - 120 °C (dec.))[17, 18] (Found: C, 17.1; H, 3.9; Cl, 25.8; N, 20.8. Calc. for $C_2H_5ClN_2O_3$. C, 17.1; H, 3.5; Cl, 25.2; N, 19.9%), which was extracted with diethyl ether (3 x 100 cm^3) and dried at 30 °C/ 0.3 mm Hg.

2. Interaction of anti 1-Chloro-1,2-ethanedionedioxime with Pyridine

anti 1-Chloro-1,2-ethanedionedioxime (1.22 g, 10 mmol) and pyridine (0.79 g, 10 mmol) in acetone (50 cm^3) were stirred at 20 °C (2 h). Removal of the solvent from the mixture afforded 1,2-dihydroxyiminoethane-N-pyridinium chloride (1.87 g, 93%) m.p., 105 - 107 °C (Found: C, 41.2; H, 3.8; Cl, 17.9; N, 20.4. $C_7H_8ClN_3O_2$ requires: C, 41.7; H, 4.0; Cl, 17.6; N, 20.8%), which was washed with diethyl ether

(2 x 50 cm^3) and dried at 30 ^oC/ 0.3 mm Hg.

3. Reaction of 1,2-Dichloro-1,2-ethanedionedioxime with Octacarbonyldicobalt(0), and Preparation of 1,2-Dihydroxy-1,2-di(N-pyridinium) Tetrachlorocobaltate(II)

1,2-Dichloro-1,2-ethanedionedioxime (4.63 g, 29 mmol) and octacarbonyldicobalt(0) (2.52 g, 7 mmol) in deoxygenated tetrahydrofuran (230 cm^3) under nitrogen were heated under reflux (6 h). The solid remaining after removal of the solvent from the mixture was washed with diethyl ether (2 x 50 cm^3) to give a brown residue (3.61 g) (Found: C, 9.9; H, 2.1; Co, 23.4; N, 7.6%) (ill-defined i.r.), which was dried at 30 ^oC/ 0.3 mm Hg.

A portion of the brown residue (0.54 g) and pyridine (1.47 g) in tetrahydrofuran (130 cm^3) were heated under reflux (4 h). Removal of the solvent from the cold mixture afforded green 1,2-dihydroxy-1,2-di(N-pyridinium) tetrachlorocobaltate(II) (0.86 g, 93%) m.p., 180 - 182 ^oC (Found: C, 33.4; H, 2.8; Cl, 31.1; Co, 13.6; N, 12.1. $C_{12}H_{12}Cl_4CoN_4O_2$ requires: C, 32.4; H, 2.7; Cl, 31.9; Co, 13.2; N, 12.6%), which was washed with acetone (2 x 50 cm^3), diethyl ether (2 x 50 cm^3) and dried at 50 ^oC/ 0.3 mm Hg.

4. Reaction of 1,2-Dichloro-1,2-ethanedionedioxime with Tetracarbonylnickel(0), and Preparation of 1,2-Dihydroxy-1,2-di(N-pyridinium) Tetrachloronickelate(II)

1,2-Dichloro-1,2-ethanedionedioxime (3.14 g, 20 mmol) and tetracarbonylnickel(0) (10.95 g, 64 mmol) in deoxygenated diethyl ether (350 cm^3) under nitrogen were stirred at 20 °C (3 d). Filtration of the mixture afforded a yellow residue (4.92 g) (Found: C, 9.4; H, 2.0; Cl, 33.2; N, 8.6; Ni, 24.9%) (ill-defined i.r.), which was washed with diethyl ether (2 x 100 cm^3) and dried at 30 °C/ 0.3 mm Hg.

A portion of the yellow residue (0.20 g) and pyridine (0.98 g) in acetone (50 cm^3) were heated under reflux (2 h). Filtration of the hot mixture afforded nickel(II) chloride dipyridine (0.10 g, 40%) (Found: C, 41.3; H, 3.4; Cl, 24.3; N, 9.5; Ni, 20.0. Calc. for $C_{10}H_{10}Cl_2N_2Ni$: C, 41.7; 3.5; Cl, 24.7; N, 9.7; Ni, 20.4%), which was washed with acetone (2 x 50 cm^3) and dried at 50 °C/ 0.3 mm Hg. Removal of the solvent from the combined filtrate and washings afforded green 1,2-dihydroxy-1,2-di(N-pyridinium) tetrachloronickelate(II) (0.11 g, 28%) m.p., 212 - 214 °C (Found: C, 31.9; H, 2.7; Cl, 30.9; N, 12.9; Ni, 12.7. $C_{12}H_{12}Cl_4N_4NiO_2$ requires: C, 32.4; H, 2.7; Cl, 31.9; N, 12.6; Ni, 13.2%), which was washed with acetone (2 x 50 cm^3), diethyl ether (2 x 50 cm^3) and dried at 50 °C/ 0.3 mm Hg.

5. Reaction of 1,2-Dichloro-1,2-ethanedionedioxime with Copper(II) Acetate Monohydrate, and Preparation of 1,2-Dihydroxy-1,2-(N-dipyridinium) Tetrachlorocuprate(II) Dipyridine

1,2-Dichloro-1,2-ethanedionedioxime (1.60 g, 10 mmol) and copper(II) acetate monohydrate (1.02 g, 5 mmol) in methanol (170 cm^3) were stirred at 20 ^oC (24 h). Filtration of the mixture afforded a green solid A (0.21 g) (Found: C, 9.2; H, 1.5; Cu, 35.2; N, 9.8%) (ill-defined i.r.), which was washed with diethyl ether (2 x 100 cm^3) and dried at 30 ^oC/ 0.3 mm Hg. The solid remaining after removal of the solvent from the combined filtrate and washings afforded a residue, which was washed with diethyl ether (2 x 100 cm^3) to give a light green residue B (0.65 g) (Found: C, 9.0; H, 2.0; Cl, 33.7; Cu, 34.1; N, 9.1%) (ill-defined i.r.). Removal of the solvent from the ethereal extracts gave unreacted 1,2-dichloro-1,2-ethanedionedioxime (0.80 g, 50% recovery) m.p., 198 - 200 ^oC (lit., 198 - 199 ^oC)[18] (identified by i.r.).

A portion of the light green residue B (0.50 g) and pyridine (1.96 g) in acetone (50 cm^3) were heated under reflux (2 h). Filtration of the mixture afforded copper(II) chloride dipyridine (0.19 g, 25%) (Found: C, 39.6; H, 3.4; Cl, 24.8; Cu, 22.0; N, 9.3. Calc. for $C_{10}H_{10}Cl_2CuN_2$: C, 41.0; H, 3.4; Cl, 24.3; Cu, 21.7; N, 9.6%), which was washed with acetone (2 x 50 cm^3) and dried at 50 ^oC/ 0.3 mm Hg. Removal

of the solvent from the filtrate afforded green 1,2-dihydroxy-1,2-(N-dipyridinium) tetrachlorocuprate(II) dipyridine (0.84 g, 55%) m.p., 196 - 198 °C (Found: C, 43.9; H, 4.1; Cl, 23.1; Cu, 11.2; N, 14.0. $C_{22}H_{22}Cl_4CuN_6O_2$ requires: C, 43.5; H, 3.6; Cl, 23.4; Cu, 10.5; N, 13.8%), which was washed with acetone (2 x 50 cm^3), diethyl ether (2 x 50 cm^3) and dried at 50 °C/ 0.3 mm Hg.

6. Interaction of amphi 1-Chloro-1,2-ethanedionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

amphi 1-Chloro-1,2-ethanedionedioxime (1.22 g, 10.0 mmol) and hydrated metal(II) acetate (5 mmol) in aqueous methanol (50%, 100 cm^3) were stirred at 20 °C (24 h). Filtration afforded:

(i) for the nickel system,
yellow-light green 1,2-di(1-chloro-1,2-ethanedionedioximato)-nickel(II) (0.95 g, 63%) (Found: C, 15.3; H, 1.6; Cl, 23.7; N, 18.4; Ni, 19.0. $C_4H_4Cl_2N_4NiO_4$ requires: C, 15.9; H, 1.3; Cl, 23.5; N, 18.6; Ni, 19.4%), which was extracted with methanol (Soxhlet), washed with water (2 x 100 cm^3) and dried at 30 °C/ 0.3 mm Hg.

(ii) for the copper(II) system,
a green residue (1.32 g) (Found: C, 10.5; H, 2.9; Cl, 23.7; Cu, 29.4; N, 9.6%) (ill-defined i.r.).

7. Treatment of 1,2-Di(1-chloro-1,2-ethanedionedioximato)-nickel(II) with Hydrochloric Acid

Dilute hydrochloric acid (2 mol dm^{-3}, ca. 1 cm^3) was added to 1,2-di(1-chloro-1,2-ethanedionedioximato)nickel(II) (0.50 g, 2 mmol) in water (50 cm^3), and the resulting mixture stirred at 20 °C (1/2 h). Extraction with diethyl ether (2 x 50 cm^3) gave anti 1-chloro-1,2-ethanedionedioxime (0.11 g, 28%) m.p., 144 - 146 (lit., 147 °C)[18] (identified by i.r.), which was washed with water (2 x 50 cm^3) and dried at 40 °C/ 0.3 mm Hg.

8. Interaction of anti 1-Chloro-1,2-ethanedionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

anti 1-Chloro-1,2-ethanedionedioxime (1.22 g, 10 mmol) and nickel(II) acetate tetrahydrate (1.24 g, 5 mmol) in aqueous methanol (50%, 100 cm^3) were stirred at 20 °C (24 h). Filtration of the mixture afforded a brown residue (1.03 g) (ill-defined i.r.).

Similarly, anti 1-chloro-1,2-ethanedionedioxime (1.22 g, 10 mmol) and copper(II) acetate monohydrate (1.00 g, 5 mmol) in aqueous methanol (50%, 100 cm^3) were stirred at 20 °C (24 h) to give a green residue (0.87 g) (ill-defined i.r.).

9. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with Hydrated Nickel(II) Chloride in the Presence of Hydrochloric Acid

a) In 1:2 molar ratio.

1,2-Diamino-1,2-ethanedionedioxime (0.24 g, 2 mmol) and nickel(II) chloride hexahydrate (0.24 g, 1 mmol) in aqueous methanol (50%, 50 cm^3) were stirred at 60 ^oC (10 min). Hydrochloric acid (2 mol dm^{-3}) was added to the resulting blue solution (pH 2). Removal of the solvent from the mixture afforded blue bis(1,2-diamino-1,2-ethanedionedioxime)-nickel(II) chloride (0.31 g, 86%) (Found: C, 13.0; H, 3.5; Cl, 19.1; N, 30.1; Ni, 16.0. $C_4H_{12}Cl_2N_8NiO_4$ requires: C, 13.1; H, 3.3; Cl, 19.4; N, 30.6; Ni, 16.0%), which was recrystallised from ethanol and dried at 30 ^oC/ 0.3 mm Hg.

b) In 1:1 molar ratio.

1,2-Diamino-1,2-ethanedionedioxime (0.24 g, 2 mmol) and nickel(II) chloride hexahydrate (0.48 g, 2 mmol) in aqueous methanol (50%, 50 cm^3) were stirred at 60 ^oC (10 min). Hydrochloric acid (2 mol dm^{-3}) was added to the resulting blue solution (pH 2). Removal of the solvent from the mixture afforded green mono(1,2-diamino-1,2-ethanedionedioxime)-nickel(II) chloride (0.22 g, 61%) (Found: C, 9.5; H, 2.5; Cl, 28.3; N, 22.0; Ni, 23.8. $C_2H_6Cl_2N_4NiO_2$ requires: C, 9.7; H, 2.4; Cl, 28.7; N, 22.6; Ni, 23.7%), which was washed with ethanol (2 x 25 cm^3) and dried at 30 ^oC/ 0.3 mm Hg.

10. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with 3-Nitroaniline

a) In the absence of sodium carbonate.

1,2-Dichloro-1,2-ethanedionedioxime (1.57 g, 10 mmol) and 3-nitroaniline (5.52 g, 40 mmol) in toluene:diethyl ether (1:1) (200 cm^3) were heated under reflux (24 h). Removal of the solvent from the mixture afforded a residue which was washed with dichloromethane (2 x 50 cm^3) to give unreacted 1,2-dichloro-1,2-ethanedionedioxime (1.52 g, 97% recovery) m.p., 198 - 200 °C (lit., 198 - 199 °C)[18] (identified by i.r.).

b) In the presence of sodium carbonate.

1,2-Dichloro-1,2-ethanedionedioxime (1.64 g, 10 mmol) in dichloromethane (100 cm^3) was shaken with sodium carbonate (11.0 g, 104 mmol) in water (100 cm^3) at -70 °C. The organic phase was separated, dried with sodium sulphate at -70 °C, and added to a solution of 3-nitroaniline (2.68 g, 19.4 mmol) in dichloromethane (100 cm^3) at -70 °C. The resultant mixture was allowed to warm up to ambient temperature (24 h). Filtration of the mixture afforded brown 1,2-di(3-nitrophenyl-N-amino)-1,2-ethanedionedioxime (1.54 g, 41%) m.p., 210 - 212 °C (Found: C, 45.8; H, 3.2; N, 23.7. $C_{14}H_{12}N_6O_6$ requires: C, 46.7; H, 3.3; N, 23.3%), which was washed with ethanol (50 cm^3) and dried at 40 °C/ 0.3 mm Hg.

11. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Ethylenediamine, and Preparation of 2,3-Dioximino-piperazine

a) 1,2-Dichloro-1,2-ethanedionedioxime (1.57 g, 10 mmol) and ethylenediamine (0.60 g, 10 mmol) in ethanol (40 cm^3) were stirred at 20 ^oC (1 h). Filtration of the mixture afforded 2,3-dioximino-piperazine dihydrochloride (2.01 g, 93%) m.p., 260 - 263 ^oC (Found: C, 22.3; H, 4.3; Cl, 32.3; N, 25.8. $C_{10}Cl_2N_4O_2$ requires: C, 22.1; H, 4.6; Cl, 32.7; N, 25.8%), which was washed with ethanol (50 cm^3) and dried at 40 ^oC/ 0.3 mm Hg.

b) 2,3-Dioximino-piperazine dihydrochloride (1.08 g, 5 mmol) and propylene oxide (12.0 g, 207 mmol) in methanol (50 cm^3) were stirred at 20 ^oC (1/2 h). Addition of water (250 cm^3) to the mixture gave yellow 2,3-dioximino-piperazine (0.58 g, 81%) m.p., 201 - 202 ^oC (lit., 203 - 205 ^oC)[19] (Found: C, 33.0; H, 5.5; N, 38.6. Calc. for $C_4H_8N_4O_2$: C, 33.3; H, 5.6; N, 38.9%), which was washed with water (2 x 50 cm^3), diethyl ether (2 x 50 cm^3) and dried at 40 ^oC/ 0.3 mm Hg.

12. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Piperazine

1,2-Dichloro-1,2-ethanedionedioxime (1.57 g, 10 mmol) and

piperazine (0.92 g, 10 mmol) in ethanol (300 cm^3) were stirred at 0 °C (2 h). Filtration of the mixture afforded pale cream 1,2-dipiperazine-1,2-ethanedionedioxime dihydrochloride (0.96 g, 57%) m.p., 188 - 190 °C (Found: C, 36.8; H, 6.5; Cl, 21.2; N, 26.1. $C_{10}H_{22}Cl_2N_6O_2$ requires: C, 36.5; H, 6.7; Cl, 21.6; N, 25.5%), which was washed with diethyl ether (2 x 50 cm^3) and dried at 40 °C/ 0.3 mm Hg.

13. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Ethylene bisacetamide

1,2-Dichloro-1,2-ethanedionedioxime (3.14 g, 20 mmol) and ethylene bisacetamide (2.88 g, 20 mmol) in ethanol (100 cm^3) were stirred in the presence of sodium hydrogen carbonate (5.0 g, 60 mmol) at 0 °C (4 h). Removal of the solvent from the mixture gave a residue which was washed with water (2 x 100 cm^3) and diethyl ether (2 x 100 cm^3) to give unreacted ethylene bisacetamide (2.77 g, 96% recovery) m.p., 170 - 172 °C (lit., 172 - 173 °C)[12] (identified by i.r.).

14. Interaction of 1,-Dichloro-1,2-ethanedionedioxime with Disodium Ethane-bis-Nitraminate

1,2-Dichloro-1,2-ethanedionedioxime (0.77 g, 5 mmol) and disodium ethane-bis-nitraminate (0.96 g, 5 mmol) in acetone (100 cm^3) were stirred at 20 °C (2 h). Filtration of the

mixture gave a residue which was washed with acetone (2 x 50 cm^3) to give disodium ethane-bis-nitraminate (0.90 g, 94% recovery) (Found: Na, 23.5. Calc. for $C_2H_4N_4Na_2O_4$: Na, 23.7%) (identified by i.r.).

15. Interaction of Oxalyl Chloride with Disodium Ethane-bis-Nitraminate

Oxalyl chloride (0.73 g, 6 mmol) and disodium ethane-bis-nitraminate (0.90 g, 5 mmol) in diethyl ether (150 cm^3) were stirred at 20 °C under nitrogen (24 h). Filtration of the mixture gave sodium chloride (0.50 g, 93%) (Found: Cl, 60.5. Calc. for ClNa: Cl, 60.7%) (identified by i.r.). Removal of the solvent from the filtrate gave white N,N'-dinitro-ethyleneoxamide (0.38 g, 40%) m.p., 178 - 180 °C (lit., 180 - 185 °C)[12] (Found: C, 22.8; H, 1.9; N, 27.1. Calc. for $C_4H_4N_4O_6$: C, 23.5; H, 2.0; N, 27.5%), which was washed with water (50 cm^3) and dried at 40 °C/ 0.3 mm Hg.

16. Interaction of N,N'-Dinitroethyleneoxamide with Hydroxylammonium Chloride and Sodium Hydroxide

Hydroxylammonium chloride (0.28 g, 4 mmol) in water (15 cm^3) was neutralised with sodium hydroxide (0.16 g, 4 mmol) in water (15 cm^3), and the resulting solution was added to N,N'-dinitroethyleneoxamide (0.40 g, 2 mmol) in methanol (30 cm^3). The resulting mixture was heated under

reflux (3 h). Removal of the solvent from the mixture afforded a residue (0.51 g) (multi-component by t.l.c.), which was washed with methanol (25 cm^3).

*17. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with 5C-substituted Tetrazoles (CHN_4X: X= H, OH, NH_2)

1,2-Dichloro-1,2-ethanedionedioxime (1.57 g, 10 mmol) and the 5C-substituted tetrazole (CHN_4X) (20 mmol) were stirred in methanol (100 cm^3) at 20 °C (24 h). Removal of the solvent from the mixture gave a residue which was washed with diethyl ether (2 x 100 cm^3) to give the unreacted 5C-substituted tetrazole (Table 5.1), which was identified by i.r. In each case, removal of the solvent from the combined ethereal extracts and washings gave 1,2-dichloro-1,2-ethanedionedioxime, m.p., 198 - 200 °C (lit., 198 - 199 °C)[18] (identified by i.r.).

Table 5.1

X	Amount of tetrazole used (g)	Amount of tetrazole recovered (g) [%]
H	1.40	1.37 (g) [98%]
OH	1.72	1.66 (g) [96%]
NH_2	1.70	1.66 (g) [98%]

*18. Interaction of anti 1-Chloro-1,2-ethanedionedioxime with 5C-substituted Tetrazoles (CHN_4X: X= H, OH, NH_2)

anti 1-Chloro-1,2-ethanedionedioxime (1.22 g, 10 mmol) and the 5C-substituted tetrazole (CHN_4X) (10 mmol) in methanol (100 cm^3) were stirred at 20 °C (24 h). Removal of the solvent from the mixture gave a residue which was washed with diethyl ether (2 x 100 cm^3) to give the unreacted 5C-substituted tetrazole (Table 5.2), which was identified by i.r. In each case, removal of the solvent from the combined ethereal extracts and washings gave anti 1-chloro-1,2-ethanedionedioxime, m.p., 144 - 146 °C (dec.) (lit., 147 °C (dec.))[18] (identified by i.r.).

Table 5.2

X	Amount of tetrazole used (g)	Amount of tetrazole recovered (g) [%]
H	0.70 (g)	0.65 (g) [93%]
OH	0.86 (g)	0.84 (g) [98%]
NH_2	0.85 (g)	0.78 (g) [92%]

*19. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Tetrazole

i) At 20 °C.

1,2-Dichloro-1,2-ethanedionedioxime (4.71 g, 30 mmol), and

tetrazole (4.14 g, 58 mmol) were added to a solution of sodium ethoxide (0.2 M, 300 cm^3), and the mixture was stirred at 20 °C (24 h). Filtration of the mixture gave sodium chloride (3.15 g, 90%) (Found: Cl, 60.4. Calc. for ClNa: Cl, 60.7%) (identified by i.r.). Removal of the solvent from the filtrate afforded white 1,2-di(5-tetrazolato)-1,2-ethanedionedioxime (2.22 g, 33%) m.p., 154 - 156 °C (Found: C, 22.0; H, 1.8; N, 60.8. $C_4H_4N_{10}O_2$ requires: C, 21.4; H, 1.8; N, 62.5%), which was washed with diethyl ether (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

ii) At -78 °C.

1,2-Dichloro-1,2-ethanedionedioxime (4.71 g, 30 mmol), and tetrazole (4.14 g, 58 mmol) were added to a solution of sodium ethoxide (0.2 M, 300 cm^3), and the mixture was stirred at -78 °C (24 h). Filtration of the mixture gave sodium chloride (3.29 g, 94%) (Found: Cl, 60.5. Calc. for ClNa: Cl, 60.7%) (identified by i.r). Removal of the solvent from the filtrate afforded white 1,2-di(5-tetrazolato)-1,2-ethanedionedioxime (3.25 g, 48%) m.p., 154 - 156 °C (identified by i.r.).

*20. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Sodium 5-Chlorotetrazolate Dihydrate

1,2-Dichloro-1,2-ethanedionedioxime (4.71 g, 30 mmol), and sodium 5-chlorotetrazolate dihydrate (9.21 g, 60 mmol) in

methanol (100 cm^3) were stirred at 20 °C (24 h). Filtration of the mixture gave sodium chloride (3.38 g, 90%) (Found: Cl, 60.6. Calc. for ClNa: Cl, 60.7%) (identified by i.r.). Removal of the solvent from the filtrate afforded white 1,2-di(5-chlorotetrazolato)-1,2-ethanedionedioxime (7.60 g, 86%) m.p., 166 - 168 °C (Found: C, 17.3; H, 0.5; N, 48.4. $C_4H_2Cl_2N_{10}O_2$ requires: C, 16.4; H, 0.7; N, 47.8%), which was washed with diethyl ether (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*21. Interaction of 1,2-Dichloro-1,2-ethanedionedioxime with Sodium 5-Nitrotetrazolate Dihydrate

1,2-Dichloro-1,2-ethanedionedioxime (0.68 g, 4 mmol), and sodium 5-nitrotetrazolate dihydrate (1.49 g, 8 mmol) in acetone (100 cm^3) were allowed to stand at -78 °C (24 h). Removal of the solvent from the cold mixture gave a residue which was washed with acetone (2 x 50 cm^3) to give sodium 5-nitrotetrazolate dihydrate (1.48 g, 98% recovery) (Found: Na, 13.0; Calc. for $CH_4N_5NaO_4$: Na, 13.3%) (identified by i.r.).

*22. Interaction of anti 1-Chloro-1,2-ethanedionedioxime with Tetrazole

anti 1-Chloro-1,2-ethanedionedioxime (2.45 g, 20 mmol), and tetrazole (1.40 g, 20 mmol) were added to a solution of

sodium ethoxide (0.07 M, 300 cm^3), and the mixture was stirred at -78 °C (24 h). Filtration of the mixture gave sodium chloride (1.01g, 86%) (Found: Cl, 60.3. Calc. for ClNa: Cl, 60.7%) (identified by i.r.). Removal of the solvent from the filtrate afforded white 1-(5-tetrazolato)-1,2-ethanedionedioxime (2.20 g, 70%) m.p., 150 - 152 °C (Found: C, 22.7; H, 3.2; N, 52.3. $C_3H_4N_6O_2$ requires: C, 23.1; H, 2.6; N, 53.8%), which was washed with diethyl ether (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*23. Interaction of anti 1-Chloro-1,2-ethanedionedioxime with Sodium 5-Chlorotetrazolate Dihydrate

anti 1-Chloro-1,2-ethanedionedioxime (0.70 g, 6 mmol) and sodium 5-chlorotetrazolate dihydrate (0.92 g, 6 mmol) in methanol (120 cm^3) were stirred at -78 °C (24 h). Filtration of the mixture gave sodium chloride (0.32 g, 97%) (Found: Cl, 60.7. Calc. for ClNa: Cl, 60.7%) (identified by i.r.). Removal of the solvent from the filtrate afforded white 1-(5-chlorotetrazolato)-1,2-ethanedionedioxime (0.99 g, 92%) m.p., 190 - 192 °C (Found: C, 18.3; H, 1.1; N, 43.5. $C_3H_3ClN_6O_2$ requires: C, 18.9; H, 1.6; N, 44.1%), which was washed with diethyl ether (2 x 50 cm^3), water (2 x 50 cm^3) and dried at 40 °C.

24. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with 2,4,6-Trinitrochlorobenzene

1,2-Diamino-1,2-ethanedionedioxime (2.07 g, 18 mmol) and 2,4,6-trinitrochlorobenzene (4.33 g, 18 mmol) in methanol (100 cm^3) were heated under reflux (48 h). Filtration of the cold mixture gave 1,2-di(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioxime (0.12 g, 2%) m.p., 250 - 252 °C (dec.) (lit., 150 °C)[8] (identified by i.r.). Removal of the solvent from the filtrate afforded orange 1-amino-2-(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioxime (1.73 g, 30%) m.p., 148 - 150 °C (Found: C, 29.0; H, 1.9; N, 29.2. $C_8H_7N_7O_8$ requires: C, 29.2; H, 2.1; N, 29.8%), which was washed with diethyl ether (2 x 50 cm^3) and dried at 25 °C/ 0.3 mm Hg.

25. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with 2,4-Dinitrochlorobenzene

1,2-Diamino-1,2-ethanedionedioxime (1.18 g, 10 mmol) and 2,4-dinitrochlorobenzene (4.05 g, 20 mmol) in methanol (100 cm^3) were heated under reflux (4 d). Removal of the solvent from the mixture afforded yellow 1-amino-2-(2,4-dinitrophenyl-N-amino)-1,2-ethanedionedioxime (1.05 g, 37%) m.p., 174 - 176 °C (Found: C, 32.9; H, 3.3; N, 28.8. $C_8H_8N_6O_6$ requires: C, 33.8; H, 2.8; N, 29.6%), which was washed with diethyl ether (2 x 100 cm^3), water (2 x 100 cm^3)

and dried at 30 °C/ 0.3 mm Hg.

26. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with Mononitrochlorobenzenes (2-, 3-, 4-)

1,2-Diamino-1,2-ethanedionedioxime (1.18 g, 10 mmol), the isomeric mononitrochlorobenzene (3.15 g, 20 mmol), and sodium hydrogen carbonate (5.0 g, 60 mmol) in methanol (150 cm^3) were heated under reflux (7 d). Filtration of each mixture gave sodium hydrogen carbonate (ca. 5 g) and a yellow filtrate. In each case, removal of the solvent from the filtrate gave a residue which was washed with diethyl ether (2 x 100 cm^3) to give unreacted 1,2-diamino-1,2-ethanedionedioxime, m.p., 196 - 198 °C (lit., 203 °C)[2] (identified by i.r.). Removal of the solvent from each set of washings gave the corresponding isomeric mononitrochlorobenzene (identified by i.r.) (Table 5.3).

Table 5.3

Mononitrochlorobenzene Isomer	Amount recovered
3-	3.01 g (96%)
4-	3.12 g (99%)
5-	2.95 g (94%)

27. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with Benzaldehyde

1,2-Diamino-1,2-ethanedionedioxime (3.50 g, 30 mmol) and benzaldehyde (6.12 g, 57 mmol) in methanol (100 cm^3) under nitrogen were heated under reflux (48 h). Filtration of the cold mixture afforded white 1-amino-2-(benzyl-N-imino)-1,2-ethanedionedioxime (5.8 g, 65%) m.p., 209 - 211 ^oC (Found: C, 52.8; H, 5.0; N, 27.8. $C_9H_{10}N_4O_2$ requires: C, 52.4; H, 4.8; N, 27.2%), which was washed with water (2 x 100 cm^3), methanol (2 x 100 cm^3) and dried at 40 ^oC/ 0.3 mm Hg.

28. Interactions of 1,2-Diamino-1,2-ethanedionedioxime with Tetrazolone

1,2-Diamino-1,2-ethanedionedioxime (1.18 g, 10 mmol), and tetrazolone (1.70 g, 20 mmol) in methanol (150 cm^3) were heated under reflux (7 d). Filtration of the mixture gave unreacted 1,2-diamino-1,2-ethanedionedioxime (1.14 g, 97% recovery) m.p., 196 - 198 ^oC (lit., 203 ^oC)[2] (identified by i.r.).

29. Interaction of 1,2-Di(phenyl-N-amino)-1,2-ethanedione-dioxime with Hydrated Metal(II) Chloride ($MCl_2.nH_2O$: M=Ni, n=6; M=Cu, n= 2)

1,2-Di(phenyl-N-amino)-1,2-ethanedionedioxime (0.81 g, 3 mmol) and hydrated metal(II) chloride (1.5 mmol) in methanol (50 cm^3) were stirred at 20 °C (1/2 h). Aqueous ammonia (0.88 s.g.) was added until precipitation was complete. Filtration afforded:

i) for the nickel(II) system,
brown bis(1,2-di(phenyl-N-amino)-1,2-ethanedionedioximato)-nickel(II) (0.80 g, 89%) m.p., 260 - 262 °C (Found: C, 55.8; H, 4.1; N, 17.8; Ni, 9.2. $C_{28}H_{26}N_8NiO_4$ requires: C, 56.3; H, 4.4; N, 18.8; Ni, 9.8%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

ii) for the copper(II) system,
a green residue (0.65 g) (ill-defined i.r.).

30. Interaction of 1,2-Di(3-nitrophenyl-N-amino)-1,2-ethane-dionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

1,2-Di(3-nitrophenyl-N-amino)-1,2-ethanedionedioxime (0.45 g, 1 mmol) and hydrated metal(II) acetate (0.5 mmol) in methanol (100 cm^3) were heated under reflux (4 h). Filtration

afforded:

i) for the nickel(II) system,
orange bis(1,2-di(3-nitrophenyl-N-amino)-1,2-ethanedione-dioximato)nickel(II) (0.46 g, 95%) m.p., 292 - 294 °C (dec.) (Found: C, 43.6; H, 2.4; N, 21.1; Ni, 8.3. $C_{28}H_{22}N_{12}NiO_{12}$ requires: C, 43.2; H, 2.8; N, 21.6; Ni, 7.6%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

ii) for the copper(II) system,
brown bis(1,2-di(3-nitrophenyl-N-amino)-1,2-ethanedione-dioximato)copper(II) (0.38 g, 78%) m.p., 268 - 270 °C (dec.) (Found: C, 42.2; H, 2.3; Cu, 8.7; N, 22.0. $C_{28}H_{22}CuN_{12}O_{12}$ requires: C, 43.0; H, 2.8; Cu, 8.1; N, 21.5%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

31. Interaction of 1-Amino-2-(2,4-dinitrophenyl-N-amino)-1,2-ethanedionedioxime with Hydrated Metal(II) Chloride ($MCl_2.nH_2O$: M= Ni, n= 6; M= Cu, n= 2)

1-Amino-2-(2,4-dinitrophenyl-N-amino)-1,2-ethanedionedioxime (1.42 g, 5 mmol) and hydrated metal(II) chloride (2.5 mmol) in methanol (100 cm^3) were heated under reflux (48 h). Filtration afforded:

i) for the nickel(II) system,
orange-brown bis(1-amino-2-(2,4-dinitrophenyl-N-amino)-1,2-

ethanedionedioximato)nickel(II) (0.86 g, 55%) m.p., 260 - 262 °C (dec.) (Found: C, 29.4; H, 2.4; N, 25.8; Ni, 8.4. $C_{16}H_{14}N_{12}NiO_{12}$ requires: C, 30.7; H, 2.2; N, 26.9; Ni, 9.4%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

ii) for the copper(II) system,
green bis(1-amino-2-(2,4-dinitrophenyl-N-amino)-1,2-ethanedionedioximato)copper(II) (0.61 g, 39%) m.p., 215 - 218 °C (dec.) (Found: C, 29.8; H, 2.5; Cu, 10.3; N, 26.0. $C_{16}H_{14}CuN_{12}O_{12}$ requires: C, 30.5; H, 2.2; Cu, 10.1; N, 26.7%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

32. Interaction of 1-Amino-2-(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

1-Amino-2-(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioxime (0.55 g, 2 mmol) and hydrated metal(II) acetate (1 mmol) in methanol (100 cm^3) were heated under reflux (3 h). Filtration afforded:

i) for the nickel(II) system,
bis(1-amino-2-(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioximato)nickel(II) (0.41 g, 68%) m.p., 223 - 225 °C (dec.) (lit., 205 °C (dec.))[8] (identified by i.r.), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and

dried at 40 °C/ 0.3 mm Hg.

ii) for the copper(II) system,
a green residue (0.33 g) (ill-defined i.r.).

33. Interaction of 1-Amino-2-(benzyl-N-imino)-1,2-ethanedionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

1-Amino-2-(benzyl-N-imino)-1,2-ethanedionedioxime (1.20 g, 6 mmol) and hydrated metal(II) acetate (3 mmol) in methanol (100 cm^3) were heated under reflux (6 h). Filtration afforded:

i) for the nickel(II) system,
burgundy bis(1-amino-2-(benzyl-N-imino)-1,2-ethanedionedioximato)nickel(II) (1.30 g, 94%) m.p., 200 - 201 °C (dec.) (Found: C, 45.9; H, 3.8; N, 23.3; Ni, 12.3. $C_{18}H_{18}N_8NiO_4$ requires: C, 46.1; H, 3.8; N, 23.9; Ni, 12.5%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

ii) for the copper(II) system,
brown bis(1-amino-2-(benzyl-N-imino)-1,2-ethanedionedioximato)copper(II) (1.32 g, 96%) m.p., 212 - 214 °C (dec.) (Found: C, 45.3; H, 3.9; Cu, 13.8; N, 22.8. $C_{18}H_{18}CuN_8O_4$ requires: C, 45.6; H, 3.8; Cu, 13.4; N, 23.6%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

34. Interaction of 2,3-Dioximino-piperazine with Hydrated Metal(II) Chloride ($MCl_2.nH_2O$: M= Ni, n= 6; M= Cu, n=2)

2,3-Dioximino-piperazine (1.44 g, 10 mmol) and hydrated metal(II) chloride (5 mmol) in methanol (100 cm^3) were stirred at 20 ^oC (1 h). Aqueous ammonia (0.88 s.g.) was added until precipitation was complete. Filtration afforded:

i) for the nickel(II) system,
brown bis(2,3-dioximato-piperazine)nickel(II) (1.39 g, 80%) (Found: C, 27.1; H, 4.1; N, 32.0; Ni, 16.7. $C_8H_{14}N_8NiO_4$ requires: C, 27.8; H, 4.1; N, 32.5; Ni, 17.0%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 ^oC/ 0.3 mm Hg.

ii) for the copper(II) system,
brown-green bis(2,3-dioximato-piperazine)copper(II) (1.22 g, 69%) (Found: C, 27.0; H, 4.1; Cu, 18.4; N, 31.4. $C_8H_{14}CuN_8O_4$ requires: C, 27.5; H, 4.0; Cu, 18.2; N, 32.0%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 ^oC/ 0.3 mm Hg.

*35. Interaction of 1,2-Di(5-tetrazolato)-1,2-ethanedione-dioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.H_2O$: M= Ni, n= 4; M= Cu, n= 1)

1,2-Di(5-tetrazolato)-1,2-ethanedionedioxime (0.90 g, 4 mmol) and hydrated metal(II) acetate (2 mmol) in aqueous methanol (90%, 200 cm^3) were stirred at 20 °C (3 h). Filtration afforded:

i) for the nickel(II) system,
light green mono(1,2-di(5-tetrazolato)-1,2-ethanedione-dioximato)nickel(II) dihydrate (0.54 g, 85 %) m.p., 173 - 175 °C (dec.) (Found: C, 14.7; H, 2.2; N, 44.0; Ni, 19.2. $C_4H_6N_{10}NiO_4$ requires: C, 15.2; H, 1.9; N, 44.2; Ni, 18.5%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

ii) for the copper(II) system,
dark green mono(1,2-di(5-tetrazolato)-1,2-ethanedione-dioximato)copper(II) dihydrate (0.40 g, 62 %) m.p., 120 - 123 °C (dec.) (Found: C, 14.3; H, 1.8; Cu, 20.1; N, 43.1. $C_4H_6CuN_{10}O_4$ requires: C, 14.9; H, 1.9; Cu, 19.8; N, 43.5%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*36. Interaction of 1,2-Di(5-chlorotetrazolato)-1,2-ethanedionedioxime with Hydrated Metal(II) Acetate ($M(OAc)_2.nH_2O$: M= Ni, n= 4; M= Cu, n= 1)

1,2-Di(5-chlorotetrazolato)-1,2-ethanedionedioxime (1.06 g, 4 mmol) and hydrated metal(II) acetate (2 mmol) in aqueous methanol (90%, 200 cm^3) were stirred at 20 °C (3 h). Filtration afforded:

i) for the nickel(II) system,
brown-green mono(1,2-di(5-chlorotetrazolato)-1,2-ethanedionedioximato)nickel(II) dihydrate (0.29 g, 42 %) m.p., 148 - 150 °C (dec.) (Found: C, 12.1; H, 1.4; N, 36.7; Ni, 14.7. $C_4H_4Cl_2N_{10}NiO_4$ requires: C, 12.4; H, 1.0; N, 36.3; Ni, 15.2%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

ii) for the copper(II) system,
green mono(1,2-di(5-chlorotetrazolato)-1,2-ethanedionedioximato)copper(II) dihydrate (0.31 g, 44%) m.p., 130 - 133 °C (dec.) (Found: C, 12.4; H, 0.8; Cu, 16.6; N, 35.1. $C_4H_4Cl_2CuN_{10}O_4$ requires: C, 12.3; H, 1.0; Cu, 16.3; N, 35.8%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*37. Interaction of 1-(5-Tetrazolato)-1,2-ethanedionedioxime with Copper(II) Acetate Monohydrate

1-(5-Tetrazolato)-1,2-ethanedionedioxime (0.62 g, 4 mmol) and copper(II) acetate monohydrate (0.40 g, 2 mmol) in aqueous methanol (90%, 200 cm^3) were stirred at 20 °C (3 h). Filtration of the mixture afforded brown-green mono(1-(5-tetrazolato)-1,2-ethanedionedioximato)copper(II) dihydrate (0.44 g, 87%) m.p., 96 - 99 °C (dec.) (Found: C, 14.6; H, 2.0; Cu, 25.6; N, 32.7. $C_3H_6CuN_6O_4$ requires: C, 14.2; H, 2.4; Cu, 25.0; N, 33.1%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*38. Interaction of 1-(5-Chlorotetrazolato)-1,2-ethanedionedioxime with Copper(II) Acetate Monohydrate

1-(5-Chlorotetrazolato)-1,2-ethanedionedioxime (1.30 g, 7 mmol) and copper(II) acetate monohydrate (0.68g, 3.5 mmol) in aqueous methanol (90%, 200 cm^3) were stirred at 20 °C (3 h). Filtration of the mixture afforded brown mono(1-(5-chloro-tetrazolato)-1,2-ethanedionedioximato)-copper(II) dihydrate (0.68 g, 69%) m.p., 146 - 148 °C (dec.) (Found: C, 11.7; H, 1.8; Cu, 22.4; N, 28.8. $C_3H_5ClCuN_6O_4$ requires: C, 12.5; H, 1.7; Cu, 22.0; N, 29.2%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C.

*39. Interaction of the Complexes of the Tetrazolato-Substituted Dioximes with Sulphuric Acid

Concentrated sulphuric acid (2 cm^3) was added to the complex of the tetrazolyl-substituted dioxime (ca. 0.5 g) in water (50 cm^3), and the mixture stirred further (2 h). Filtration of the mixture gave the free protonated ligand, which was washed with water (2 x 50 cm^3), and dried in air (Table 5.4).

Table 5.4

R	R'	Metal	Amount of complex used, g	Amount of protonated ligand obtained, g (%)
H	tH	Cu	0.52	0.22 (69)
H	tCl	Cu	0.47	0.12 (39)
tH	tH	Ni	0.59	0.23 (56)
tH	tH	Cu	0.55	0.24 (63)
tCl	tCl	Ni	0.46	0.10 (29)
tCl	tCl	Cu	0.45	0.16 (48)

40. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-nickel(II) with Acetic Anhydride

a) Under nitrogen.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.60 g, 2 mmol) and acetic anhydride (162.3 g, 1590 mmol) were stirred at 20 ^oC under nitrogen (7 d). Filtration of the

mixture gave unreacted bis(1,2-diamino-1,2-ethanedione-dioximato)nickel(II) (0.54 g, 90% recovery), m.p., 300 - 302 °C (dec.) (lit., 306 °C (dec.))[8] (identified by i.r.).

b) In the presence of moisture.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.60 g, 2 mmol) and acetic anhydride (162.3 g, 1590 mmol) were stirred at 20 °C (48 h). Removal of the solvent from the mixture afforded a residue which was washed with diethyl ether (2 x 100 cm^3) to give nickel(II) acetate tetrahydrate (0.24 g, 67%) (Found: Ni, 23.3; Calc. for $C_4H_{14}NiO_8$: Ni, 23.6%) (identified by i.r.). Removal of the solvent from the ethereal extracts gave crystalline 1,2-diamino-1,2-ethane-dionedioxime diacetate (0.61 g, 73%) m.p., 190 - 192 °C (lit., 193 - 194 °C)[20] (identified by i.r.).

41. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-nickel(II) with Acetyl Chloride

a) In 1:4 molar ratio.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.58 g, 2 mmol) and acetyl chloride (0.63 g, 8.0 mmol) in diethyl ether (50 cm^3) were stirred at 20 °C under nitrogen (24 h). Filtration of the mixture gave unreacted bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.56 g, 97% recovery) m.p., 300 - 302 °C (dec.) (lit., 306 °C (dec.))[8] (identified

by i.r.).

b) With excess acetyl chloride.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.58 g, 2 mmol) and acetyl chloride (55.2 g, 703 mmol) were stirred at 20 °C under nitrogen (48 h). Filtration of the mixture afforded a purple-brown residue (0.62 g) (multi-component by t.l.c.). Removal of the solvent from the filtrate afforded a white residue (0.54 g) (multi-component by t.l.c.).

42. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-nickel(II) with 2,4,6-Trinitrochlorobenzene

a) In the absence of sodium bicarbonate.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.58 g, 2 mmol) and 2,4,6-trinitrochlorobenzene (1.99 g, 8 mmol) in methanol (100 cm^3) were stirred at 20 °C (3 d). Filtration of the mixture gave bis(1-amino-2-(2,4,6-trinitophenyl-N-amino)-1,2-ethanedionedioximato)nickel(II) (0.12 g, 5%) m.p., 223 - 225 °C (dec.) (lit., 205 °C (dec.))[8] (identified by i.r.). Removal of the solvent from the filtrate afforded mono(1,2-diamino-1,2-ethanedionedioxime)nickel(II) chloride (0.44 g, 17%) (Found: C, 9.6; H, 3.0; Cl, 28.0; N, 22.1; Ni, 23.0. $C_2H_6Cl_2N_4NiO_2$ requires: C, 9.7; H, 2.4; Cl, 28.7; N, 22.6; Ni, 23.7%) (identified by i.r.), which was washed with acetone (100 cm^3) and dried at 40 °C/ 0.3 mm Hg. Removal of the solvent from the filtrate gave 1-amino-2-(2,4,6-trinitro-

phenyl-N-amino)-1,2-ethanedionedioxime (0.94 g, 37%) m.p., 185 - 187 °C (identified by i.r.), which was washed with diethyl ether (2 x 50 cm^3) and dried at 40 °C/ 0.3 mm Hg. Removal of the solvent from the ethereal extracts gave unreacted 2,4,6-trinitrochlorobenzene (0.91 g, 35%) m.p., 70 - 71 °C (lit., 73 °C)[21] (identified by i.r.).

b) In the presence of sodium bicarbonate.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (2.30 g, 8 mmol), 2,4,6-trinitrochlorobenzene (7.82 g, 32 mmol) and sodium hydrogen carbonate (3 g, 28 mmol) were stirred in methanol (100 cm^3) (24 h). Filtration of the mixture gave a residue which was washed with methanol (3 x 100 cm^3). Removal of the solvent from the methanol washings afforded a solid which was separated by column chromatography (silica gel). Elution with toluene gave unreacted 2,4,6-trinitrochlorobenzene (3.41 g, 34%) m.p., 70 - 71 °C (lit., 73 °C)[21] (identified by i.r.), and elution with methanol gave bis(1-amino-2-(2,4,6-trinitro-phenyl-N-amino)-1,2-ethanedionedioximato)nickel(II) (2.83 g, 28%) m.p., 223 - 225 °C (dec.) (lit., 205 °C (dec.))[8] (identified by i.r.).

43. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-copper(II) Monohydrate with 2,4,6-Trinitrochloro-benzene

Bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) mono-

hydrate (1.20 g, 4 mmol) and 2,4,6-trinitrochlorobenzene (3.86 g, 16 mmol) in methanol (200 cm^3) were heated under reflux (48 h). Removal of the solvent from the mixture afforded green mono(1-amino-2-(2,4,6-trinitrophenyl-N-amino)-1,2-ethanedionedioxime)copper(II) chloride (1.69 g, 34%) (Found: C, 21.0; H, 2.2; Cl, 15.8; Cu, 13.1; N, 21.0. $C_8H_7Cl_2CuN_7O_8$ requires: C, 20.7; H, 1.5; Cl, 15.3; Cu, 13.7; N, 21.1%), which was washed with diethyl ether (3 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg. Removal of the solvent from the ethereal extracts gave unreacted 2,4,6-trinitrochlorobenzene (2.71 g, 55% recovery) m.p., 70 - 71 °C (lit., 73 °C)[21] (identified by i.r.).

44. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-metal(II) ($M(dagH)_2.nH_2O$: M= Ni, n= 0; M= Cu, n= 1) with 2,4-Dinitrochlorobenzene

Bis(1,2-diamino-1,2-ethanedionedioximato)metal(II) (3 mmol) and 2,4-dinitrochlorobenzene (2.43 g, 12 mmol) in methanol (100 cm^3) were heated under reflux (7 d). Filtration gave:

i) for the nickel(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.84 g, 95% recovery) m.p., 300 - 302 °C (dec.) (lit., 306 °C (dec.))[8] (identified by i.r.).

ii) for the copper(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)copper(II)

monohydrate (0.93 g, 98 % recovery) m.p., 196 - 198 °C (dec.) (lit., 200 °C (dec.)[8] (identified by i.r.).

45. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-metal(II) ($M(daqH)_2.nH_2O$: M= Ni, n=0; M=Cu, n=1) with 2-Nitrochlorobenzene

Bis(1,2-diamino-1,2-ethanedionedioximato)metal(II) (3 mmol) and 2-nitrochlorobenzene (1.89 g, 12 mmol) in methanol (100 cm^3) were heated under reflux (7 d). Filtration gave:

i) for the nickel(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.81 g, 92% recovery) m.p., 300 - 302 °C (dec.) (lit., 306 °C (dec.))[8] (identified by i.r.).

ii) for the copper(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate (0.87 g, 97 % recovery) m.p., 196 - 198 °C (dec.) (lit., 200 °C (dec.)[8] (identified by i.r.).

46. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-metal(II) ($M(dagH)_2.nH_2O$: M= Ni, n= 0; M= Cu, n= 1) with Benzaldehyde

Bis(1,2-diamino-1,2-ethanedionedioximato)metal(II) (3 mmol) and benzaldehyde (1.27 g, 12 mmol) in methanol (100 cm^3) were heated under reflux (7 d). Filtration gave:

i) for the nickel(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.80 g, 90% recovery) m.p., 300 - 302 °C (dec.) (lit., 306 °C (dec.))[8] (identified by i.r.).

ii) for the copper(II) system,
unreacted bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate (0.88 g, 93% recovery) m.p., 196 - 198 °C (dec.) (lit., 200 °C (dec.)[8] (identified by i.r.).

*47. Interaction of Bis(1,2-diamino-1,2-ethanedione-dioximato)nickel(II) with 5-Hydroxytetrazole

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.58 g, 2 mmol) and 5-hydroxytetrazole (0.69 g, 8 mmol) in pyridine (50 cm^3) were heated at 70 °C (1 h). Filtration of the mixture afforded purple tetrapyridinebis(5-hydroxy-tetrazolato)nickel(II) (0.84 g, 78%) (Found: C, 48.0; H, 4.7; N, 31.3; Ni, 10.3. $C_{22}H_{22}N_{12}NiO_2$ requires: C, 48.5; H, 4.0; N, 30.8 ;Ni, 10.8%), which was washed with methanol

(2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C. Removal of the solvent from the filtrate gave 1,2-diamino-1,2-ethanedionedioxime (0.36 g, 78%) m.p., 196 - 198 °C (lit., 203 °C)[2] (identified by i.r.).

*48. Interaction of Bis(1-chloro-1,2-ethanedionedioximato)-nickel(II) with Sodium 5-Nitrotetrazolate Dihydrate

Bis(1-chloro-1,2-ethanedionedioximato)nickel(II) (0.30 g, 1 mmol) and sodium 5-nitrotetrazolate dihydrate (0.34 g, 2 mmol) in water (100 cm^3) were heated under reflux (24 h). Filtration of the mixture afforded pink tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) (0.18 g, 64%) (Found: C, 6.9; H, 1.8; N, 39.4; Ni, 16.5. $C_2H_8N_{10}NiO_8$ requires: C, 6.7; H, 2.2; N, 39.0; Ni, 16.4%), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3), recrystallised from acetone:water (1:1) (20 cm^3) and dried at 40 °C. Removal of the solvent from the filtrate afforded a beige solid (0.44 g) (multi-component by t.l.c.).

*49. Interaction of Bis(1,2-diamino-1,2-ethanedione-dioximato)nickel(II) with Sodium 5-Nitro-tetrazolate Dihydrate

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (0.29 g, 1 mmol) and sodium 5-nitrotetrazolate dihydrate (0.34 g, 2 mmol) in water (100 cm^3) were heated under reflux (24 h). Filtration of the mixture afforded pink tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) (0.11 g, 39%) (Found: Ni, 16.2. $C_2H_8N_{10}NiO_8$ requires: Ni, 16.4%), (identified by i.r.), which was washed with methanol (2 x 100 cm^3), water (2 x 100 cm^3) and dried at 40 °C. Removal of the solvent from the filtrate afforded a cream pasty solid (0.34 g) (shown by t.l.c. to consist of three components).

*50. Interaction of 5-Hydroxytetrazole with Nickel(II) Chloride Hexahydrate in Pyridine

5-Hydroxytetrazole (0.86 g, 10 mmol) and nickel(II) chloride hexahydrate (1.19 g, 5 mmol) in pyridine (50 cm^3) were stirred at 20 °C (2 h). Filtration of the mixture afforded purple tetrapyridinebis(5-hydroxytetrazolato)-nickel(II) (0.82 g, 72%) (Found: Ni, 10.3. $C_{22}H_{22}N_{12}NiO_2$ requires: Ni, 10.8%) (identified by i.r.).

*51. Interaction of Sodium 5-Nitrotetrazolate Dihydrate with Nickel(II) Chloride Hexahydrate

Sodium 5-nitrotetrazolate dihydrate (0.86 g, 5 mmol) and nickel(II) chloride hexahydrate (0.56 g, 2.5 mmol) in aqueous acetone (50%, 50 cm^3) were stirred at 20 °C (6 h). Aqueous ammonia (0.88 s.g.) was added until precipitation was complete. Filtration of the mixture afforded pink tetraaqua-(5-nitrotetrazolato-N^2)nickel(II) (0.25 g, 71%) (Found: Ni, 16.2. $C_2H_8N_{10}NiO_8$ requires: Ni, 16.4%) (identified by i.r.).

52. Interaction of 1,2-Diamino-1,2-ethanedionedioxime with Nickel(II) Chloride, and Boric Acid

a) In water.

Nickel(II) chloride hexahydrate (1.19 g, 5 mmol), 1,2-diamino-1,2-ethanedionedioxime (1.77 g, 15 mmol), and boric acid (0.62 g, 10 mmol) were stirred in water (20 cm^3) at 70 °C (15 min). Sodium tetraborate tetrahydrate (0.95 g, 3 mmol) was added slowly and the resulting mixture heated further at 70 °C (5 min). Filtration of the hot mixture afforded the orange clathrochelate $[Ni(dag)_2(B(OH)_2)_2]$ (2.10 g, 73%) (Found: C, 12.0; H, 3.9; B, 5.0; N, 29.0; Ni, 15.4. $C_4H_{12}B_2N_8NiO_8$ requires: C, 12.6; H, 3.2; B, 5.7; N, 29.4; Ni, 15.4%), which was washed with water (2 x 100 cm^3) and dried at 40 °C/ 0.3 mm Hg.

b) In ethanol.

Nickel(II) chloride hexahydrate (1.19 g, 5 mmol), 1,2-diamino-1,2-ethanedionedioxime (1.77 g, 15 mmol), and boric acid (0.62 g, 10 mmol) were stirred in ethanol (50 cm^3) at 70 °C (1/2 h). Sodium tetraborate tetrahydrate (0.95 g, 3 mmol) was added slowly, and the resulting mixture heated further at 70 °C (10 min). Filtration of the hot mixture afforded the orange clathrochelate $[Ni(dag)_2(B(OC_2H_5)_2)_2]$ (2.53 g, 73%) (Found: C, 28.8; H, 6.0; B, 4.0; N, 22.9; Ni, 11.1. $C_{12}H_{28}B_2N_8NiO_8$ requires: C, 29.2; H, 5.7; B, 4.4; N, 22.7; Ni, 11.9%), which was washed with ethanol (2 x 100 cm^3), water (2 x 100 cm^3), and dried at 40 °C/ 0.3 mm Hg.

53. Interaction of Bis(1,2-diamino-1,2-ethanedionedioximato)-nickel(II) with Boron Trifluoride Etherate

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (2.00 g, 7 mmol) in dichloromethane (25 cm^3) was added portionwise to boron trifluoride etherate (6.92 g, 49 mmol), and the mixture stirred at 20 °C (18 h). Filtration of the mixture afforded the orange clathrochelate $[Ni(dag)_2(BF_2)_2]$ (2.62 g, 98%) (Found: C, 11.4; H, 2.6; B, 5.4; N, 27.9; Ni, 14.7. $C_4H_8B_2F_4N_8NiO_4$ requires: C, 12.4; H, 2.1; B, 5.6, N, 28.8; Ni, 15.1%), which was washed with water (2 x 50 cm^3), diethyl ether (2 x 50 cm^3) and dried at 40 °C/ 0.3 mm Hg.

54. Interaction of Dimethyl Acetylenedicarboxylate with Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II)

a) At 20 °C.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (2.93 g, 10 mmol) and dimethyl acetylenedicarboxylate (5.68 g, 40 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were stirred at 20 °C (3 d). Filtration of the mixture afforded a brown residue A (0.95 g) (Found: Ni, 22.1%). The filtrate was evaporated to dryness under nitrogen and acetone was added (40 cm^3). Filtration of the resulting precipitate afforded residue A (1.73 g) (Found: Ni, 22.2%) (identified by i.r.). Addition of petroleum ether (b.p., 40/60 °C, 150 cm^3) to the acetone extracts afforded white 4,5-diamino fused N-hydroxypyrrole-2,3,6,7-tetracarboxylate (4.1 g, 51%) m.p., 136 - 138 °C (Found: C, 42.0; H, 4.8; N, 13.3. $C_{14}H_{18}N_4O_{10}$ requires: C, 41.8; H, 4.5; N, 13.9%), which was extracted with diethyl ether (2 x 50 cm^3). This was purified by column chromatography (silica gel) using cyclohexane:toluene as the eluting solvent and dried in air.

b) Under reflux.

Bis(1,2-diamino-1,2-ethanedionedioximato)nickel(II) (2.93 g, 10 mmol) and dimethyl acetylenedicarboxylate (5.68 g, 40 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (2 h). Filtration of the mixture afforded a brown residue A (0.87 g) (Found: Ni, 22.1%). The

filtrate was evaporated to dryness under nitrogen and acetone was added (40 cm^3). Filtration of the resulting precipitate afforded residue A (1.82 g) (Found: Ni, 22.1%) (identified by i.r.). Addition of petroleum ether (b.p., 40/60 ^oC, 150 cm^3) to the acetone extracts afforded white 4,5-diamino fused N-hydroxypyrrole-2,3,6,7-tetracarboxylate (2.0 g, 25%) m.p., 136 - 138 ^oC (identified by i.r.).

55. Interaction of Dimethyl Acetylenedicarboxylate with Bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) Monohydrate

a) At 20 ^oC.

Bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate (0.50 g, 1.5 mmol) and dimethyl acetylenedicarboxylate (0.9 g, 6 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were stirred at 20 ^oC (6 d). Filtration of the mixture gave unreacted bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate (0.48 g, 96% recovery) m.p., 195 - 197 ^oC (dec.) (lit., 200 ^oC (dec.))[8] (identified by i.r.).

b) Under reflux.

Bis(1,2-diamino-1,2-ethanedionedioximato)copper(II) monohydrate (0.50 g, 1.5 mmol) and dimethyl acetylenedicarboxylate (0.9 g, 6 mmol) in aqueous 1,2-dimethoxyethane

(12.5%, 80 cm^3) were heated under reflux (5 h). Filtration of the hot mixture afforded a green residue B (0.48 g) (Found: Cu, 23.7%). The filtrate was evaporated to dryness under nitrogen, and acetone was added (50 cm^3). Addition of petroleum ether (b.p., 40/60 ^oC, 200 cm^3) to the acetone extracts afforded white 4,5-diamino fused N-hydroxy-pyrrole-2,3,6,7-tetracarboxylate (0.33 g, 26%) m.p., 136 - 138 ^oC (identified by i.r.), which was extracted with diethyl ether (2 x 50 cm^3) and dried in air.

56. Interaction of Dimethyl Acetylenedicarboxylate with the 1:1 and the 1:2 Nickel Chloride Adducts of Diamino-1,2-ethanedionedioxime

Bis(1,2-diamino-1,2-ethanediondioxime)nickel(II) chloride (1.58 g, 4 mmol) and dimethyl acetylenedicarboxylate (2.34 g, 16 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Filtration of the hot mixture gave unreacted bis(1,2-diamino-1,2-ethanedionedioxime)nickel(II) chloride (1.52 g, 96% recovery) (Found: Ni, 16.4; Calc. for $C_4H_{12}N_8NiO_8$: Ni, 16.0%) (1.52 g, 96% recovery) (identified by i.r.).

Similarly, mono(1,2-diamino-1,2-ethanedionedioxime)nickel(II) chloride (1.23 g, 5 mmol) failed to react with dimethyl acetyledicarboxylate (1.42 g, 10 mmol) under the conditions specified above.

57. Interaction of Dimethyl Acetylenedicarboxylate with 1,2-Diamino-1,2-ethanedionedioxime

1,2-Diamino-1,2-ethanedionedioxime (0.59 g, 5 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (24 h). Removal of the solvent from the mixture gave a paste (1.86 g). Addition of diethyl ether (100 cm^3) to the paste at 0 °C afforded a precipitate (multi-component by t.l.c.).

58. Interaction of Dimethyl Acetyledicarboxylate with Bis(1,2-diphenyl-1,2-ethanedionedioximato)copper(II)

a) At 20 °C.

Bis(1,2-diphenyl-1,2-ethanedionedioximato)copper(II) (0.51 g, 1 mmol) and dimethyl acetylenedicarboxylate (0.52 g, 4 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were stirred at 20 °C (6 d). Filtration of the mixture gave bis(1,2-diphenyl-1,2-ethanedionedioximato)copper(II) (0.47 g, 92% recovery) (Found: Cu, 11.5; Calc. for $C_{28}H_{22}CuN_4O_4$: Cu, 11.7%) (identified by i.r.).

b) Under reflux.

Bis(1,2-diphenyl-1,2-ethanedionedioximato)copper(II) (0.51 g, 1 mmol) and dimethyl acetylenedicarboxylate (0.52 g, 4 mmol)

in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 h). Filtration of the hot mixture afforded a green residue C (0.21 g) (Found: C, 21.5; H, 0.5; Cu, 28.3; N, 0.7%). The filtrate was evaporated to dryness under nitrogen, and acetone was added (50 cm^3). Addition of diethyl ether (200 cm^3) to the acetone extracts gave white 4,5-diphenyl fused N-hydroxypyrrole 2,3,6,7-tetracarboxylate (0.36 g, 37%) m.p., 98 - 100 °C (Found: C, 49.6; H, 4.8; N, 4.7. $C_{26}H_{24}N_2O_{10}$ requires: C, 50.4; H, 4.6; N, 5.3%). This was purified by column chromatography (silica gel) using cyclohexane:toluene as the eluting solvent and dried in air.

59. Interaction of Dimethyl Acetylenedicarboxylate with Bis(1,2-diphenyl-1,2-ethanedionedioximato)nickel(II)

a) At 20 °C.

Bis(1,2-diphenyl-1,2-ethanedionedioximato)nickel(II) (0.48 g, 1 mmol) and dimethyl acetylenedicarboxylate (0.52 g, 4 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were stirred at 20 °C (6 d). Filtration of the mixture gave bis(1,2-diphenyl-1,2-ethanedionedioximato)nickel(II) (0.47 g, 98% recovery) (Found: Ni, 10.5; Calc. for $C_{28}H_{22}N_4NiO_4$: Ni, 10.9%) (identified by i.r.).

b) Under reflux.

Bis(1,2-diphenyl-1,2-ethanedionedioximato)nickel(II) (0.48 g,

1 mmol) and dimethyl acetylenedicarboxylate (0.52 g, 4 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 h). Filtration of the hot mixture afforded a green residue D (0.21 g). The filtrate was evaporated to dryness under nitrogen, and acetone was added (50 cm^3). Addition of diethyl ether (200 cm^3) to the acetone extracts gave white 4,5-diphenyl fused N-hydroxypyrrole 2,3,6,7-tetracarboxylate (0.32 g, 34%) m.p., 98 - 100 °C (identified by i.r.).

60. Interaction of Dimethyl Acetylenedicarboxylate with 1,2-Diphenyl-1,2-ethanedionedioxime

1,2-Diphenyl-1,2-ethanedionedioxime (1.20 g, 5 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Removal of the solvent from the mixture gave a paste (2.51 g). Addition of diethyl ether (100 cm^3) to the paste at 0 °C gave a precipitate, which was filtered to give 1,2-diphenyl-1,2-ethanedionedioxime (1.08 g, 90% recovery) m.p., 241 - 243 °C (lit., 245 - 246 °C)[22] (identified by i.r.).

61. Interaction of Dimethyl Acetylenedicarboxylate with Bis(1,2-dimethyl-1,2-ethanedionedioximato)nickel(II)

Bis(1,2-dimethyl-1,2-ethanedionedioximato)nickel(II) (1.44 g,

5 mmol) and dimethyl acetylenedicarboxylate (2.84 g, 20 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Filtration of the hot mixture gave unreacted bis(1,2-dimethyl-1,2-ethanedionedioximato)-nickel(II) (1.38 g, 96% recovery) (Found: Ni, 20.6; Calc. for $C_8H_{14}N_4NiO_4$: Ni, 20.3%) (identified by i.r.).

62. Interaction of Dimethyl Acetylenedicarboxylate with 1,2-Dimethyl-1,2-ethanedionedioxime

1,2-Dimethyl-1,2-ethanedionedioxime (0.58 g, 5 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Removal of the solvent from the mixture gave a paste (1.83 g). Addition of diethyl ether (100 cm^3) to the paste at 0 ^oC gave a precipitate which was filtered to give 1,2-dimethyl-1,2-ethanedionedioxime (0.48 g, 83% recovery) m.p., 237 - 239 ^oC (lit., 240 - 241 ^oC)[22] (identified by i.r.).

63. Interaction of Dimethyl Acetylenedicarboxylate with Bis(cyclohexane-1,2-ethanedionedioximato)nickel(II)

Bis(cyclohexane-1,2-ethanedionedioximato)nickel(II) (1.14 g, 3 mmol) and dimethyl acetylenedicarboxylate (1.69 g, 12 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Filtration of the hot mixture gave unreacted bis(cyclohexane-1,2-ethanedionedioximato)nickel(II)

(1.07 g, 94% recovery) (Found: Ni, 17.0; Calc. for $C_{12}H_{18}N_4NiO_4$: Ni, 17.2%) (identified by i.r.).

64. Interaction of Dimethyl Acetylenedicarboxylate with Cyclohexane-1,2-ethanedionedioxime

Cyclohexane-1,2-ethanedionedioxime (0.71 g, 5 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) in aqueous 1,2-dimethoxyethane (12.5%, 80 cm^3) were heated under reflux (5 d). Removal of the solvent from the mixture gave a paste (2.96 g). Addition of diethyl ether (100 cm^3) to the paste at 0 ^oC gave a precipitate, which was filtered to give cyclohexane-1,2-ethanedionedioxime (0.60 g, 85% recovery) m.p., 180 - 182 ^oC (lit., 185 - 188 ^oC)[22] (identified by i.r.).

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APPENDIX

Table A1 Intermolecular Distances (Å) for $NiCl_2.2dagH_2$

atom1	atom2	dist	S	a	b	c
H(3)	...Ni	2.96	1	1.0	0.0	0.0
H(11a)	...Ni	3.65	-1	0.0	0.0	0.0
O(4)	...Cl(1)	3.16	1	1.0	0.0	0.0
N(4)	...Cl(1)	3.78	1	1.0	0.0	0.0
C(2)	...Cl(1)	3.56	1	1.0	0.0	0.0
H(3)	...Cl(1)	2.30	1	1.0	0.0	0.0
H(4)	...Cl(1)	2.18	1	1.0	0.0	0.0
N(11)	...Cl(1)	3.32	-1	0.0	0.0	0.0
N(21)	...Cl(1)	3.55	-1	0.0	0.0	0.0
H(21b)	...Cl(1)	2.58	-1	0.0	0.0	0.0
H(11a)	...Cl(1)	2.42	-1	0.0	0.0	0.0
N(41)	...Cl(1)	3.40	2	1.0	0.0	0.0
H(41b)	...Cl(1)	3.13	2	1.0	0.0	0.0
H(41a)	...Cl(1)	3.22	2	1.0	0.0	0.0
N(11)	...Cl(2)	3.35	2	0.0	0.0	-1.0
N(41)	...Cl(2)	3.67	2	1.0	0.0	0.0
H(41b)	...Cl(2)	3.02	2	1.0	0.0	0.0
H(11b)	...Cl(2)	2.63	2	0.0	0.0	-1.0
O(2)	...Cl(2)	3.05	-2	0.0	0.0	1.0
O(3)	...Cl(2)	3.74	-2	0.0	0.0	1.0
N(2)	...Cl(2)	3.78	-2	0.0	0.0	1.0
H(2)	...Cl(2)	3.00	-2	0.0	0.0	1.0
H(3)	...Cl(2)	3.33	-2	1.0	0.0	1.0
H(31)	...O(1)	3.02	2	0.0	0.0	0.0

C(3)	...O(1)	3.02	2	0.0	0.0	0.0
H(41a)	...O(1)	2.60	2	1.0	0.0	0.0
N(31)	...O(2)	2.97	-1	1.0	0.0	1.0
H(41b)	...O(2)	2.36	-1	1.0	0.0	1.0
H(31a)	...O(2)	2.04	-1	1.0	0.0	1.0
O(4)	...O(3)	3.20	1	1.0	0.0	0.0
N(31)	...O(3)	3.02	-1	0.0	0.0	1.0
H(31b)	...O(3)	2.20	-1	0.0	0.0	1.0
N(21)	...O(4)	3.00	-2	1.0	0.0	1.0
H(2)	...O(4)	2.61	-2	1.0	0.0	1.0
H(21a)	...O(4)	2.12	-2	1.0	0.0	1.0
N(2)	...N(11)	3.40	-1	0.0	0.0	0.0
N(21)	...N(11)	3.24	-1	1.0	0.0	0.0
H(21b)	...N(11)	2.57	-1	1.0	0.0	0.0
H(11a)	...N(2)	2.96	-1	0.0	0.0	0.0
H(31a)	...N(2)	2.95	-1	1.0	0.0	1.0
H(41a)	...N(21)	2.80	-2	1.0	1.0	1.0
H(3)	...N(3)	1.99	1	1.0	0.0	0.0
C(3)	...N(31)	3.35	-1	1.0	0.0	1.0
C(4)	...N(31)	3.31	-1	1.0	0.0	1.0
H(1)	...N(31)	2.61	2	0.0	0.0	-1.0
H(11a)	...C(2)	3.04	-1	0.0	0.0	0.0
H(31a)	...C(3)	2.96	-1	1.0	0.0	1.0
H(1)	...C(3)	3.01	2	0.0	0.0	-1.0

Symmetry Transformations: The second atom is related to the first atom, at (x, y, z), by the symmetry operation S with (a, b, c) added to the (x', y', z') of S.

where S	1	x,	y,	z
	-1	-x,	-y,	-z
	2	x,	1/2-y,	1/2+z
	-2	-x,	1/2+y,	1/2-z

Table A2 Intramolecular Distances (Å) for $NiCl_2.2dagH_2$

O(1)	...Ni	3.07	O(2)	...Ni	3.15
O(3)	...Ni	3.05	O(4)	...Ni	3.18
N(11)	...Ni	4.19	N(21)	...Ni	4.20
N(31)	...Ni	4.17	N(41)	...Ni	4.18
C(1)	...Ni	2.88	C(2)	...Ni	2.89
C(3)	...Ni	2.88	C(4)	...Ni	2.89
H(1)	...Ni	2.91	H(4)	...Ni	3.16
Cl(2)	...Cl(1)	3.57	O(3)	...Cl(1)	3.13
N(1)	...Cl(1)	3.32	N(2)	...Cl(1)	3.29
N(3)	...Cl(1)	3.14	O(1)	...Cl(2)	3.11
N(1)	...Cl(2)	3.14	N(3)	...Cl(2)	3.47
N(4)	...Cl(2)	3.14	C(4)	...Cl(2)	3.65
H(1)	...Cl(2)	2.34	N(11)	...O(1)	2.63
C(1)	...O(1)	2.24	H(11b)	...O(1)	2.34
N(21)	...O(2)	2.64	N(3)	...O(2)	3.27
C(2)	...O(2)	2.24	H(21a)	...O(2)	2.32
N(31)	...O(3)	2.64	C(3)	...O(3)	2.25
H(31b)	...O(3)	2.28	N(41)	...O(4)	2.60
C(4)	...O(4)	2.24	H(3)	...O(4)	2.95
N(41a)	...O(4)	2.20	N(11)	...N(1)	2.35
N(2)	...N(1)	2.53	N(4)	...N(1)	3.21
C(2)	...N(1)	2.32	H(1)	...N(1)	1.79
H(11b)	...N(1)	2.55	N(21)	...N(11)	2.87
H(21b)	...N(11)	2.54	C(2)	...N(11)	2.48
N(21)	...N(2)	2.34	N(3)	...N(2)	3.01
N(4)	...N(2)	3.04	C(1)	...N(2)	2.33

H(2)	...N(2)	1.99
C(1)	...N(21)	2.45
H(2)	...N(21)	2.45
C(2)	...H(21b)	2.11
N(4)	...N(3)	2.54
H(31b)	...N(3)	2.47
H(41b)	...N(31)	2.64
N(41)	...N(4)	2.35
H(4)	...N(4)	1.85
C(3)	...N(41)	2.46
C(3)	...H(41b)	2.73
H(1)	...C(1)	2.91
H(11b)	...C(1)	1.93
H(2)	...C(2)	2.47
H(31a)	...C(3)	1.99
H(31a)	...C(4)	2.60
H(41a)	...C(4)	1.95
H(21a)	...N(2)	2.56
H(11a)	...N(21)	2.51
C(1)	...H(21b)	2.66
N(31)	...N(3)	2.34
C(4)	...N(3)	2.31
N(41)	...N(31)	2.90
C(4)	...N(31)	2.47
C(3)	...N(4)	2.33
H(41a)	...N(4)	2.52
H(31a)	...N(41)	2.61
C(4)	...H(41b)	2.13
H(11a)	...C(1)	1.92
H(11a)	...C(2)	2.55
H(21a)	...C(2)	1.96
H(31b)	...C(3)	1.87
H(4)	...C(4)	2.96

Table A3 Intermolecular Distances (Å) for $Ni(tNO_2)_2 \cdot (H_2O)_4$

atom1	atom2	dist	S	a	b	c
N(4)	...Ni	4.19	3	-0.5	-0.5	-1.0
O(1)	...N(1)	2.71	3	0.0	0.0	0.0
O(1w)	...N(2)	2.99	-1	0.0	0.0	0.0
H(2w)	...N(2)	2.98	-1	0.0	0.0	0.0
O(1w)	...N(3)	3.29	-1	0.0	0.0	0.0
H(2w)	...N(3)	2.96	-1	0.0	0.0	0.0
H(2w)	...N(3)	2.42	3	-0.5	-0.5	0.0
H(2w)	...N(4)	2.87	3	-0.5	-0.5	0.0
O(1w)	...N(4)	3.29	-3	-0.5	0.5	0.0
H(1w)	...N(4)	2.19	-3	-0.5	0.5	0.0
O(1)	...C(1)	2.28	3	0.0	0.0	0.0
C(1)	...C(1)	3.48	-3	-0.5	0.5	0.0
H(1w)	...C(1)	2.96	-3	-0.5	0.5	0.0
O(2)	...O(1)	2.14	3	0.0	0.0	-1.0
H(1w)	...O(2)	2.74	-3	-0.5	0.5	0.0
O(1w)	...O(1w)	3.00	2	0.0	0.0	0.0
H(1w)	...O(1w)	2.98	2	0.0	0.0	0.0
O(1w)	...O(1w)	3.01	-2	0.0	0.0	0.0

Symmetry Transformations: The second atom is related to the first atom, at (x, y, z), by the symmetry operation S with (a, b, c) added to the (x', y', z') of S.

where S	1	x,	y,	z
	-1	-x,	-y,	-z
	2	x,	-y,	-z
	-2	-x,	y,	z
	3	x,	1/2-y,	1/2+z
	-3	-x,	-1/2+y,	-1/2-z
	4	x,	1/2+y,	1/2-z
	-4	-x,	-1/2-y,	-1/2+z

Table A4 Intramolecular Distances (Å) for $Ni(tNO_2)_2.(H_2O)_4$

N(1)	...Ni	3.04
N(3)	...Ni	3.07
N(4)	...Ni	2.22
C(1)	...Ni	4.10
H(1w)	...Ni	2.65
H(2w)	...Ni	2.88
N(3)	...N(1)	2.18
N(5)	...N(1)	2.42
O(1w)	...N(1)	3.22
H(1w)	...N(1)	2.89
C(1)	...N(2)	2.05
H(1w)	...N(2)	2.77
N(4)	...N(2)	2.16
O(1w)	...N(2)	2.99
C(1)	...N(3)	2.08
O(2)	...N(4)	2.71
N(5)	...N(4)	2.43
O(2)	...C(1)	2.28

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